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(54) POSITIVE TYPE RESIST COMPOSITION FOR ELECTRON BEAM OR X- RAY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an excellent positive type resist composition for electron beams or X-rays having high sensitivity and high resolution and giving a resist pattern whose profile is rectangular (free from a T-top shape peculiar to a resist for irradiation with electron beams).

SOLUTION: The positive type resist composition contains a compound which generates an acid when irradiated with electron beams or X-rays, a resin having the residue of a compound having a smaller ionization potential than p- ethylphenol in a group which is released by the action of the acid and having solubility in an alkali developing solution increased by the action of the acid and at least one acetal compound having a specified structure.

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[Patent number]

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## CLAIMS

[Claim(s)]

[Claim 1] (a) In the compound which generates an acid by the exposure of an electron ray or an X-ray, and the radical from which it is desorbed according to an operation of an acid (b1) Have the residue of the compound in which an ionization potential value smaller than the ionization potential value of p-ethylphenol is shown. The positive-resist constituent for an electron ray or X-rays characterized by containing a kind at least among the acetal compounds expressed with the resin to which the solubility over an alkali developer increases according to an operation of an acid and the (c) general formula (A), or a general formula (B).

[Formula 1]

a formula -- ( -- A -- ) -- or -- ( -- B -- ) -- inside -- R -- one -- ' -- and -- R -- two -- ' -- mutually-independent -- carrying out -- the organic radical of carbon numbers 1-30 -- expressing .

[Claim 2] The electron ray according to claim 1 or the positive-resist constituent for X-rays characterized by the aforementioned (b1) resin being resin which the alcoholic compound expressed with the vinyl ether compound and the following general formula (D) which are expressed with the alkali fusibility polymer which has a hydroxyl group, and the following general formula (C) is made to react under an acid catalyst, and is obtained.

[Formula 2]

R3' expresses the organic radical of carbon numbers 1-30 among a formula (C). W expresses a divalent organic radical among a formula (D). X is an organic radical and the value of the ionization potential (Ip) of HO-X is the radical which shows a value smaller than Ip value of p-ethylphenol. n expresses the integer of 0-4. when n is 2-4, even if two or more W is the same, it may differ.

[Claim 3] (a) the resin to which the solubility over an alkali developer increases according to the operation of an acid which has the compound which generates an acid by the exposure of an electron ray or an X-ray, and the repeat unit express with a formula (b2) (I), and (c) -- the electron ray characterize by to contain a kind at least among the acetal compounds express with a general formula (A) or a general formula (B) according to claim 1, or the positive-resist constituent for X-rays.

[Formula 3]

R1 expresses a hydrogen atom or a methyl group among a formula (I). R2 and R3 express a hydrogen atom or the alkyl group of carbon numbers 1-4 independently respectively. W, X, and n are synonymous with the above.

[Claim 4] The electron ray according to claim 2 or 3 or the positive-resist constituent for X-rays characterized by expressing X with a formula (II).

-L-Y (II)

L expresses single bond or an alkylene group among a formula (II). Y is [Formula 4].

The radical chosen from \*\*\*\* is expressed. R4 expresses the straight chain of carbon numbers 1-6, or the alkyl group of branching independently respectively. In the integer of 0-7, and n3, the integer of 0-9 and n4 express the integer of 0-9, and n5 expresses [ n1 / the integer of 0-3, and n2 ] the integer of 0-9.

[Claim 5] the total amount of the acetal compound (aforementioned [ c ]) -- the above (b1) -- or (b2) the electron ray according to claim 1 to 4 or the POJIREJISUTO constituent for X-rays characterized by being under the 100 weight sections more than the 0.1 weight section to the AUW of a polymer.

[Claim 6] (a) The electron ray according to claim 1 to 5 or the positive-resist constituent for X-rays characterized by the compound which generates an acid by the exposure of an electron ray or an X-ray containing at least one of the compounds expressed with a general formula (I') - (III') either.

[Formula 5]

the inside of a formula, and R1-R37 are the same -- or it differs and the shape of the shape of a hydrogen atom and a straight chain, the letter of branching or an annular alkyl group, and a straight chain, the letter of branching or an annular alkoxy group, hydroxyl, a halogen atom, or 38 -S-R are expressed. R38 expresses the shape of a straight chain, the letter of branching, an annular alkyl group, or an aryl group. Moreover, two or more of R1-R15, R16-R27, and R28-R37 may join together, and the ring containing one sort chosen from single bond, carbon, oxygen, sulfur, and nitrogen or two sorts or more may be formed. X- expresses the anion of a sulfonic acid.

## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention is excellent in the pattern profile obtained by irradiating through an electron ray or an X-ray about the positive-resist constituent for an electron ray or X-rays, and relates to the chemistry multiplier system positive-resist constituent for an electron ray or X-rays which is high resolving power in high sensitivity.

[0002]

[Description of the Prior Art] the integrated circuit is raising the degree of integration increasingly, and consists of the line breadth of a HAFUMIN cron less or equal in manufacture of semi-conductor substrates, such as a VLSI, — processing of a detailed pattern has overly come to be needed. In order to fulfill the need, operating wavelength of the aligner used for photolithography is short-wave-ized increasingly, and by the time far-ultraviolet light and excimer laser light (XeCl, KrF, ArF, etc.) are examined, now, it will become. Still more detailed pattern formation has come [ furthermore, / by the electron ray or the X-ray ] to be considered.

[0003] It is positioned as a generation's pattern formation technique one after another, and, especially as for an electron ray or an X-ray, development of the next generation or the positive type which can attain high sensitivity, high resolution, and a rectangle profile configuration, and a negative-resist constituent is desired.

[0004] Furthermore, in the case of a positive type electron ray or X ray resist, that it is [ which is put the effect of the basic pollutant in atmospheric air, or within and without irradiation equipment ] easy to be influenced (desiccation of a paint film), the front face made it refractory, and when it was the Rhine pattern, it became a T-Top configuration (a front face becomes T character-like eaves), and in the case of a contact hole pattern, there was a problem that a front face became a capping configuration (it is eaves formation to a contact hole front face). On the other hand, in order to prevent a capping configuration or a T-Top configuration, when a binder is made in hydrophilicity, there is also a problem that \*\*\*\*\* happens.

[0005]

[Problem(s) to be Solved by the Invention] The purposes of this invention are high sensitivity and high resolution, and the resist pattern profile obtained is to offer the outstanding positive-resist constituent for an electron ray or X-rays which is a rectangle (it does not become a T-top configuration peculiar to especially the resist for electron beam irradiation).

[0006]

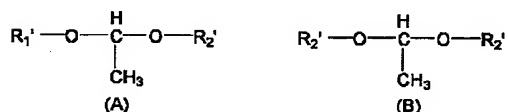
[Means for Solving the Problem] In the positive-resist constituent for an electron ray or X-rays, it found out that high performance, high resolving, and the further excellent resist pattern profile were obtained by using the polymer which includes the structure which shows  $I_p$  value lower than the ionization potential ( $I_p$ : about 8.9eV) of p-hydroxystyrene unit (p-ethylphenol) in the radical from which it is desorbed with an acid, and a specific low-molecular acetal compound as a result of examination towards high performance. That is, by this invention, the following electron ray or the positive-resist constituent for X-rays is offered, and the above-mentioned purpose is attained.

[0007] (a) In the compound which generates an acid by the exposure of an electron ray or an X-ray, and the

radical from which it is desorbed according to an operation of an acid (b1) Have the residue of the compound in which an ionization potential value smaller than the ionization potential value of p-ethylphenol is shown. The positive-resist constituent for an electron ray or X-rays characterized by containing a kind at least among the acetal compounds expressed with the resin to which the solubility over an alkali developer increases according to an operation of an acid and the (c) general formula (A), or a general formula (B).

[0008]

[Formula 6]

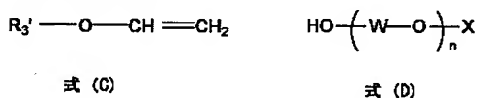


[0009] a formula -- (A) -- or -- (B) -- inside -- R -- one -- ' -- and -- R -- two -- ' -- mutually-independent -- carrying out -- the organic radical of carbon numbers 1-30 -- expressing .

(2) The positive-resist constituent for an electron ray or X-rays of the aforementioned (1) publication characterized by the aforementioned (b1) resin being resin which the alcoholic compound expressed with the vinyl ether compound and the following general formula (D) which are expressed with the alkali fusibility polymer which has a hydroxyl group, and the following general formula (C) is made to react under an acid catalyst, and is obtained.

[0010]

[Formula 7]

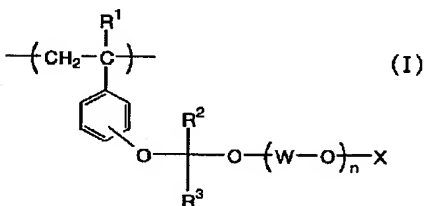


[0011] R3' expresses the organic radical of carbon numbers 1-30 among a formula (C). W expresses a divalent organic radical among a formula (D). X is an organic radical and the value of the ionization potential (Ip) of HO-X is the radical which shows a value smaller than Ip value of p-ethylphenol. n expresses the integer of 0-4. when n is 2-4, even if two or more W is the same, it may differ.

(3) -- the resin to which the solubility over an alkali developer increases according to the operation of an acid which has the compound which generates an acid by the exposure of the (a) electron ray or an X-ray, and the repeat unit expressed with a formula (b2) (I), and (c) -- the electron ray characterized by to contain a kind at least among the acetal compounds expressed with a general formula (A) or a general formula (B) according to claim 1, or the positive-resist constituent for X-rays.

[0012]

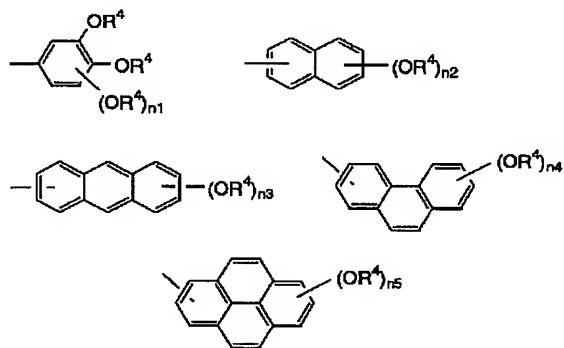
[Formula 8]



[0013] R1 expresses a hydrogen atom or a methyl group among a formula (I). R2 and R3 express a hydrogen atom or the alkyl group of carbon numbers 1-4 independently respectively. W, X, and n are synonymous with the above.

(4) The positive-resist constituent for an electron ray or X-rays the above (2) characterized by expressing X with a formula (II), or given in (3). - L-Y L expresses single bond or an alkylene group among the (II) type (II). Y is [0014].

[Formula 9]



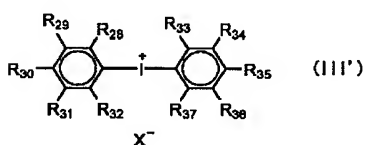
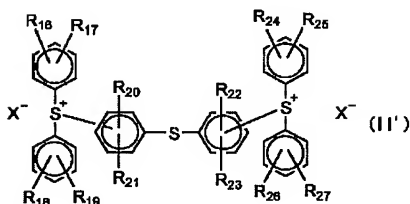
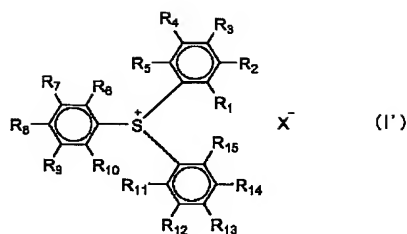
[0015] The radical chosen from \*\*\*\* is expressed. R4 expresses the straight chain of carbon numbers 1-6, or the alkyl group of branching independently respectively. In the integer of 0-7, and  $n3$ , the integer of 0-9 and  $n4$  express the integer of 0-9, and  $n5$  expresses [  $n1$  / the integer of 0-3, and  $n2$  ] the integer of 0-9.

(5) the total amount of the acetal compound (aforementioned [ c ]) -- an electron ray the above (b1) of an or (b2), and given in either of aforementioned (1) - (4) characterized by being under the 100 weight sections more than the 0.1 weight section to the AUW of a polymer, or the POJIREJISUTO constituent for X-rays.

(6) The positive-resist constituent for an electron ray or X-rays given in either of aforementioned (1) - (5) characterized by the compound which generates an acid by the exposure of the (a) electron ray or an X-ray containing at least one of the compounds expressed with a general formula (I') - (III') either.

[0016]

[Formula 10]



[0017] the inside of a formula, and R1-R37 are the same -- or it differs and the shape of the shape of a hydrogen atom and a straight chain, the letter of branching or an annular alkyl group, and a straight chain, the letter of branching or an annular alkoxy group, hydroxyl, a halogen atom, or 38 -S-R are expressed. R38 expresses the shape of a straight chain, the letter of branching, an annular alkyl group, or an aryl group. Moreover, two or more of R1-R15, R16-R27, and R28-R37 may join together, and the ring containing one sort chosen from single bond, carbon, oxygen, sulfur, and nitrogen or two sorts or more may be formed. X- expresses the anion of a sulfonic acid.

[0018] Below, a desirable mode is indicated.

(7) The shape of a straight chain by which X- was permuted by at least one fluorine atom and at least one fluorine atom, The shape of a straight chain permuted by the letter of branching or the annular alkyl group, and at least one fluorine atom, The acyl group permuted by the letter of branching or the annular alkoxy group, and at least one fluorine atom, The acyloxy radical permuted by at least one fluorine atom, the sulfonyl group permuted by at least one fluorine atom, The sulfonyloxy radical permuted by at least one fluorine atom, the sulfonylamino radical permuted by at least one fluorine atom, The aryl group permuted by at least one fluorine atom, the aralkyl radical permuted by at least one fluorine atom, And the alkoxy carbonyl group permuted by at least one fluorine atom, since -- the aforementioned (6) electron ray characterized by being the anion of the benzenesulfonic acid which has at least one selected sort, a naphthalene sulfonic acid, or an anthracene sulfonic acid, or the positive-resist constituent for X-rays.

[0019] (8) The positive-resist constituent for an electron ray or X-rays given in either of aforementioned (1) - (7) characterized by mainly including propylene-glycol-monomethyl-ether acetate as a solvent.

[0020] (9) Positive-resist constituent for an electron ray or X-rays given in either of aforementioned (1) - (8) characterized by containing (e) organic base nature compound further.

[0021] (10) Positive-resist constituent for an electron ray or X-rays given in either of aforementioned (1) - (9) characterized by containing further (f) fluorine system and/or a silicon system surfactant.

[0022]

[Embodiment of the Invention] Hereafter, the electron ray of this invention or the positive-resist constituent for X-rays (henceforth a positive type electron ray or an X ray resist constituent) is explained.

[0023] [I] Compound which generates an acid by the exposure of the (a) electron ray or an X-ray (henceforth "a component (a)")

Although anything can be used if it is the compound which generates an acid by the exposure of an electron ray or an X-ray as a component (a), the compound expressed with general formula (I') - (III') is desirable.

[0024] In general formula (I') - (III'), the thing of 1-4 carbon numbers like a methyl group, an ethyl group, a propyl group, n-butyl, sec-butyl, and t-butyl which may have a substituent is mentioned as the shape of a straight chain of R1-R38, and a letter alkyl group of branching. As an annular alkyl group, the thing of 3-8 carbon numbers like a cyclo propyl group, a cyclopentyl group, and a cyclohexyl radical which may have a substituent is mentioned. As the shape of a straight chain of R1 -R37, and a letter alkoxy group of branching, the thing of 1-4 carbon numbers like a methoxy group, an ethoxy radical, a hydroxy ethoxy radical, a propoxy group, an n-butoxy radical, an iso butoxy radical, a sec-butoxy radical, and a t-butoxy radical is mentioned, for example. As an annular alkoxy group, a cyclopenthyloxy radical and a cyclohexyloxy radical are mentioned, for example. As a halogen atom of R1 -R37, a fluorine atom, a chlorine atom, a bromine atom, and iodine atom can be mentioned. As an aryl group of R38, the thing of 6-14 carbon numbers which may have a phenyl group, a tolyl group, a methoxyphenyl radical, and a substituent like a naphthyl group, for example is mentioned.

[0025] The alkoxy group of 1-4 carbon numbers, a halogen atom (a fluorine atom, a chlorine atom, iodine atom), the aryl group of 6-10 carbon numbers, the alkenyl radical of 2-6 carbon numbers, a cyano group, a hydroxy group, a carboxy group, an alkoxy carbonyl group, a nitro group, etc. are mentioned preferably as these substituents.

[0026] Moreover, two or more of R1-R15, R16-R27, and R28-R37 can mention a furan ring, a dihydrofuran ring, a pyran ring, a trihydro pyran ring, a thiophene ring, a pyrrole ring, etc., for example as a ring containing one sort chosen from the single bond and carbon which are combined and formed, oxygen, sulfur, and nitrogen, or two sorts or more.

[0027] In general formula (I') - (III'), X- is the anion of a sulfonic acid. Furthermore, as an example, although condensation polykaryotic aromatic series sulfonic-acid anions, such as perfluoro alkane sulfonic-acid anions, such as  $\text{CF}_3\text{SO}_3^-$ , a pentafluoro benzenesulfonic acid anion, and a naphthalene-1-sulfonic-acid anion, an anthraquinone sulfonic-acid anion, a sulfonic group content color, etc. can be mentioned, it is not limited to these.

[0028] As for X-, it is more desirable that it is the anion of the benzenesulfonic acid which has at least one sort chosen from the following radical, a naphthalene sulfonic acid, or an anthracene sulfonic acid especially. at least one fluorine atom -- the shape of a straight chain permuted by one fluorine atom even if few -- the letter of branching, or an annular alkyl group -- the shape of a straight chain permuted by one fluorine atom even if few -- The letter of branching or an annular alkoxy group, if few the acyl group permuted by the fluorine atom of one \*\*, if few the acyloxy radical permuted by the fluorine atom of one \*\*, if few the sulfonyl group permuted by the fluorine atom of one \*\*, if few the sulfonyloxy radical permuted by the fluorine atom of one \*\* -- the sulfonylamino radical permuted by one fluorine atom even if few -- the aryl group permuted



by one fluorine atom even if few — even if few, one fluorine atom permuted — an aralkyl radical And the alkoxy carbonyl group permuted by at least one fluorine atom [0029] As the shape of an above-mentioned straight chain, the letter of branching, or an annular alkyl group, carbon numbers are 1–12 and what is permuted by 1–25 fluorine atoms is desirable. Specifically, a TORIFURORO methyl group, the Pentough Rollo ethyl group, 2 and 2, 2-TORIFURORO ethyl group, a heptaphloropropyl radical, a hepta-FURORO isopropyl group, perphloro butyl, a perphloro octyl radical, the perphloro dodecyl, a perphloro cyclohexyl radical, etc. can be mentioned. Especially, the perphloroalkyl group of the carbon numbers 1–4 altogether permuted with the fluorine is desirable.

[0030] As the shape of an above-mentioned straight chain, the letter of branching, or an annular alkoxy group, carbon numbers are 1–12 and what is permuted by 1–25 fluorine atoms is desirable. Specifically, a TORIFURORO methoxy group, a pen TAFURORO ethoxy radical, a hepta-FURORO isopropoxy radical, a perphloro butoxy radical, a perphloro octyloxy radical, a perphloro dodecyloxy radical, a perphloro cyclohexyloxy radical, etc. can be mentioned. Especially, the perphloro alkoxy group of the carbon numbers 1–4 altogether permuted with the fluorine is desirable.

[0031] As the above-mentioned acyl group, carbon numbers are 2–12 and what is permuted by 1–23 fluorine atoms is desirable. Specifically, the Tori Flo Roar cetyl group, the Flo Roar cetyl group, a pen TAFURORO propionyl radical, the Pentough Rollo benzoyl, etc. can be mentioned.

[0032] As the above-mentioned acyloxy radical, carbon numbers are 2–12 and what is permuted by 1–23 fluorine atoms is desirable. Specifically, a TORIFURORO acetoxy radical, a FURORO acetoxy radical, a pen TAFURORO propionyloxy radical, a pen TAFURORO benzoyloxy radical, etc. can be mentioned.

[0033] As the above-mentioned sulfonyl group, carbon numbers are 1–12 and what is permuted by 1–25 fluorine atoms is desirable. Specifically, a truffe ROROME tongue sulfonyl group, the Pentough ROROE tongue sulfonyl group, a perphloro butane sulfonyl group, a perphloro octane sulfonyl group, a pen TAFURORO benzenesulphonyl radical, 4-trifluoromethylbenzene sulfonyl group, etc. can be mentioned.

[0034] As the above-mentioned sulfonyloxy radical, carbon numbers are 1–12 and what is permuted by 1–25 fluorine atoms is desirable. Specifically, truffe ROROME tongue sulfonyloxy, a perphloro butane sulfonyloxy radical, 4-trifluoromethylbenzene sulfonyloxy radical, etc. can be mentioned.

[0035] As the above-mentioned sulfonylamino radical, carbon numbers are 1–12 and what is permuted by 1–25 fluorine atoms is desirable. Specifically, a truffe ROROME tongue sulfonylamino radical, a perphloro butane sulfonylamino radical, a perphloro octane sulfonylamino radical, a pen TAFURORO benzenesulphonyl amino radical, etc. can be mentioned.

[0036] As the above-mentioned aryl group, carbon numbers are 6–14 and what is permuted by 1–9 fluorine atoms is desirable. Specifically, Pentough Rollo phenyl group, 4-truffe ROROME chill phenyl group, hepta-FURORO naphthyl group, nona FURORO anthranil, 4-FURORO phenyl group, 2, and 4-difloro phenyl group etc. can be mentioned.

[0037] As the above-mentioned aralkyl radical, carbon numbers are 7–10 and what is permuted by 1–15 fluorine atoms is desirable. Specifically, a pen TAFURORO phenylmethyl radical, a pen TAFURORO phenylethyl radical, perphloro benzyl, a perphloro phenethyl radical, etc. can be mentioned.

[0038] As the above-mentioned alkoxy carbonyl group, carbon numbers are 2–13 and what is permuted by 1–25 fluorine atoms is desirable. Specifically, a TORIFURORO methoxycarbonyl group, a pen TAFURORO

ethoxycarbonyl radical, a pen TAFURORO phenoxy carbonyl group, a perphloro butoxycarbonyl radical, a perphloro octyloxy carbonyl group, etc. can be mentioned.

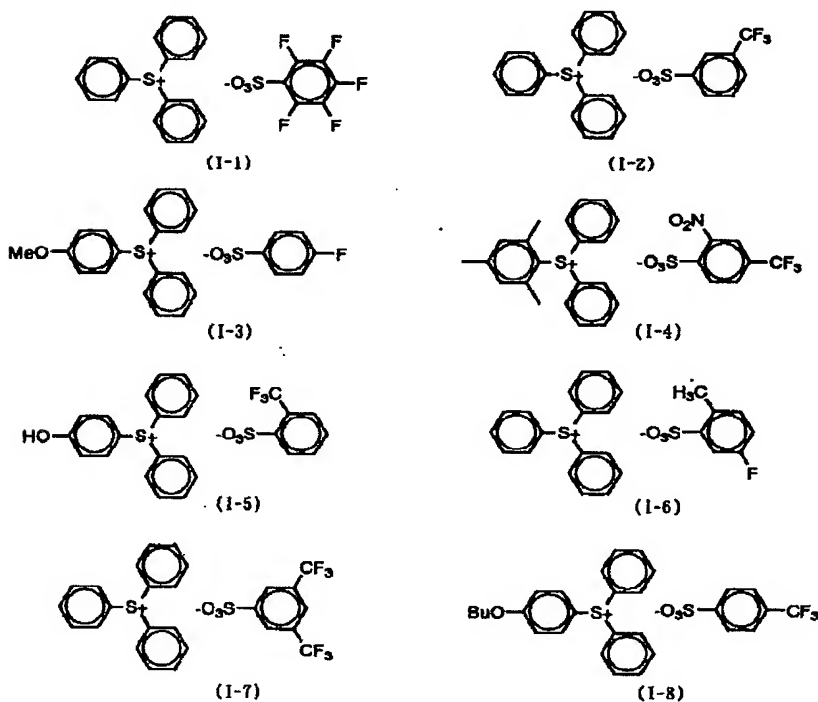
[0039] As most desirable X<sup>-</sup>, it is a fluorine permutation benzenesulfonic acid anion, and especially a pentafluoro benzenesulfonic acid anion is desirable especially.

[0040] Moreover, the benzenesulfonic acid which has the above-mentioned fluorine-containing substituent, a naphthalene sulfonic acid, or an anthracene sulfonic acid may be further permuted by the shape of a straight chain, the letter of branching or an annular alkoxy group, an acyl group, an acyloxy radical, a sulfonyl group, a sulfonyloxy radical, a sulfonylamino radical, an aryl group, an aralkyl radical, the alkoxy carbonyl group (these carbon number range is the same as that of the aforementioned thing), the halogen (except for a fluorine), the hydroxyl group, a nitro group, etc.

[0041] The example of a compound expressed with a general formula (I') is shown below.

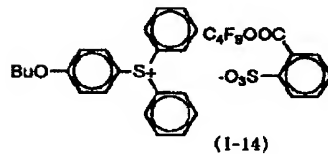
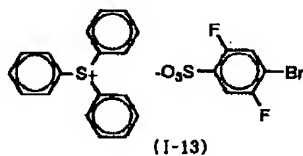
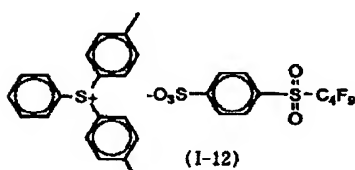
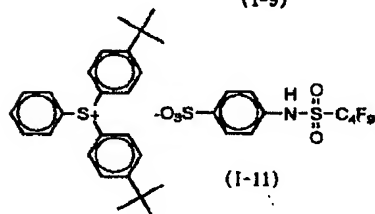
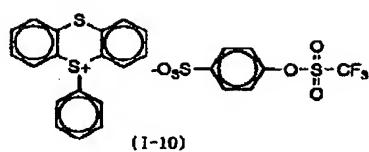
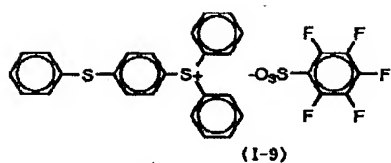
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[Formula 11]



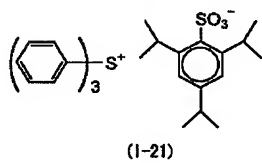
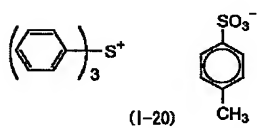
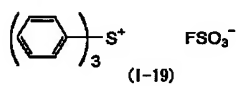
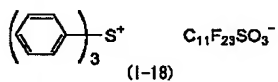
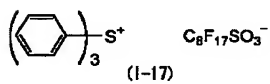
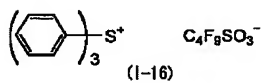
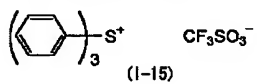
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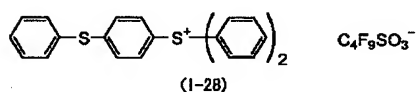
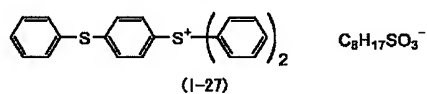
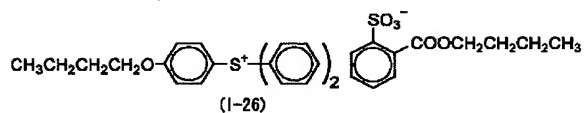
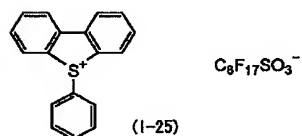
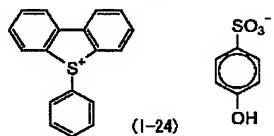
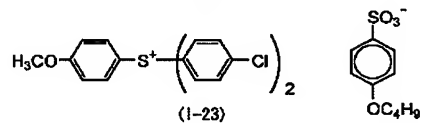
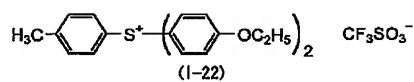
[0044]

[Formula 13]



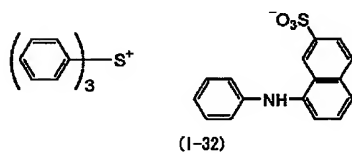
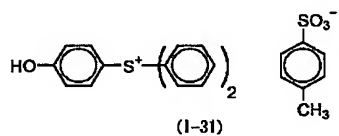
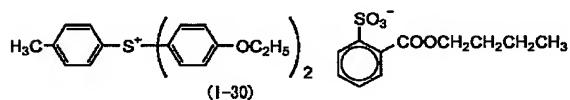
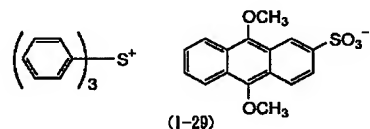
[0045]

[Formula 14]



[0046]

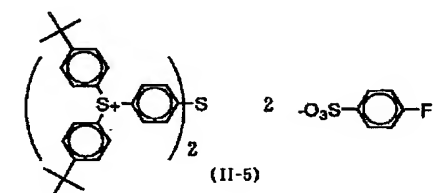
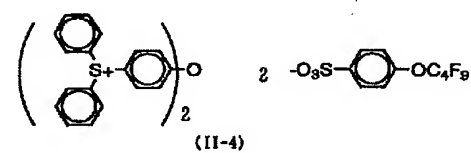
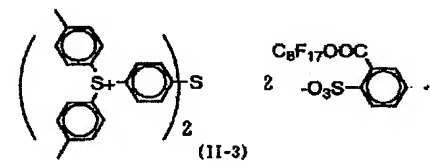
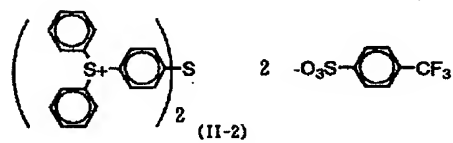
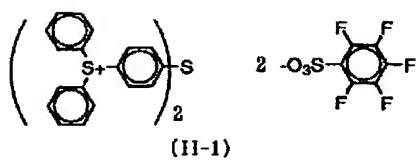
[Formula 15]



[0047] The example of a compound expressed with a general formula (II') is shown below.

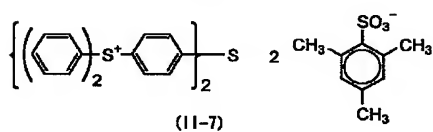
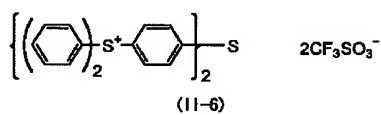
[0048]

[Formula 16]



[0049]

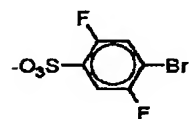
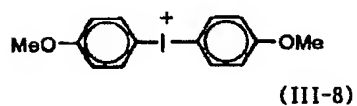
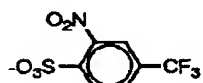
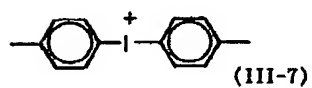
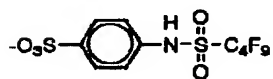
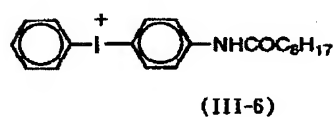
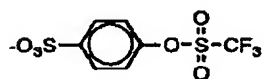
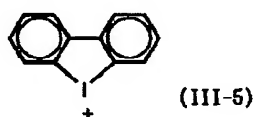
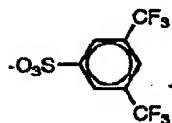
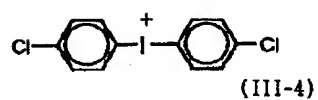
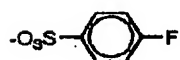
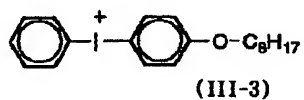
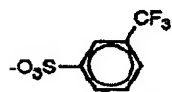
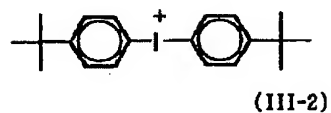
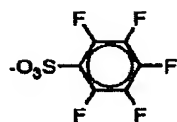
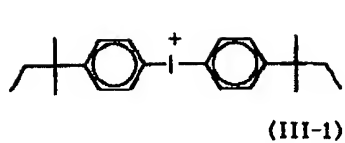
[Formula 17]



[0050] The example of a compound expressed with a general formula (III') is shown below.

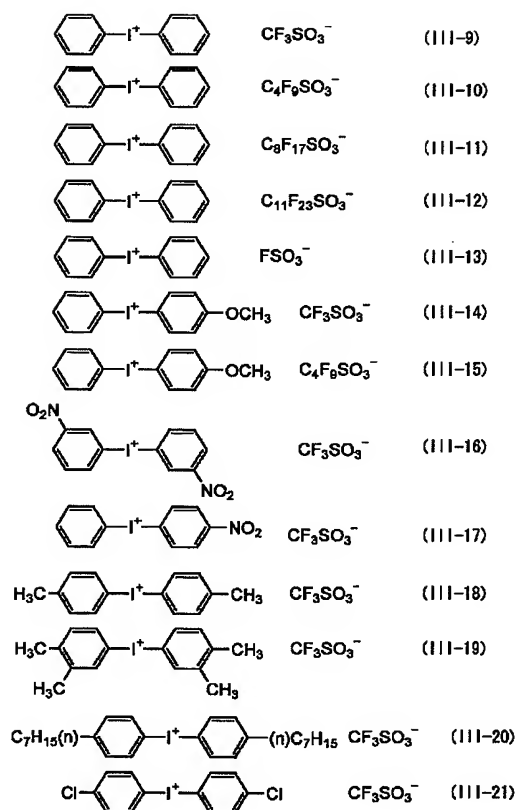
[0051]

[Formula 18]



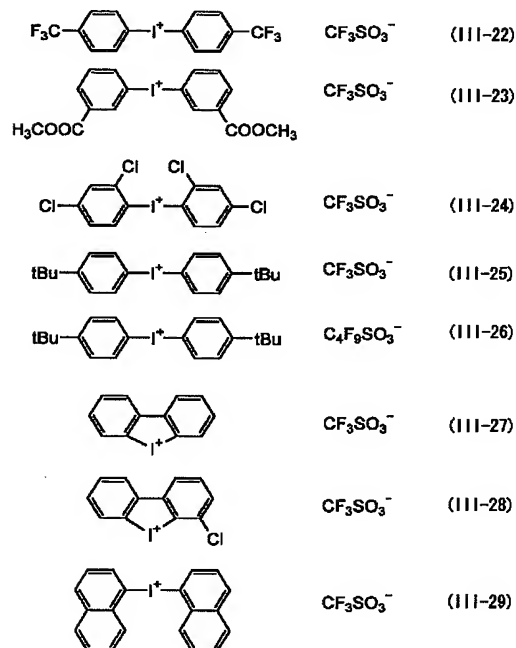
[0052]

[Formula 19]



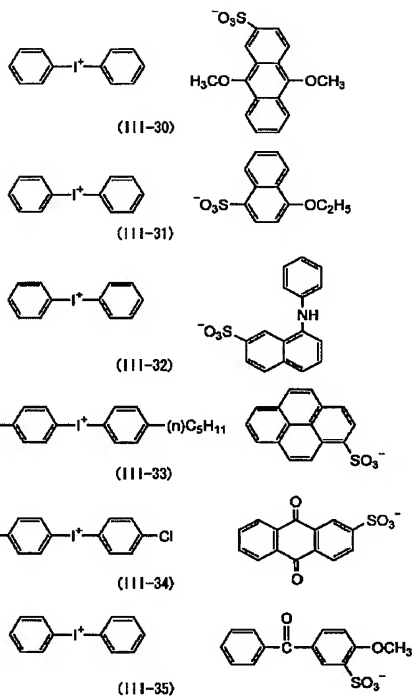
[0053]

[Formula 20]



[0054]

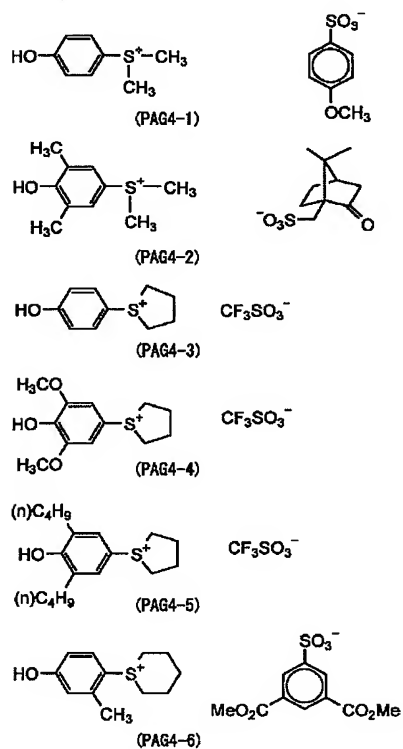
[Formula 21]



[0055] The example of acid generators other than the compound expressed with general formula (I') - (III') below is given.

[0056]

[Formula 22]



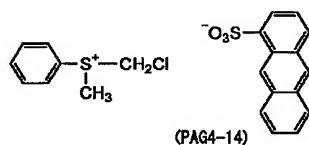
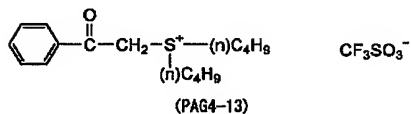
[0057]



[Formula 23]

[0058]

[Formula 24]



[0059] One sort or two sorts or more may be used together and used for the compound expressed with general formula (I') – (III').

[0060] A general formula (I') and the compound of (II') For example, aryl Grignard reagents, such as aryl magnesium bromide, How to carry out salt exchange of the triarylsulfonium halide which the phenyl sulfoxide which is not permuted [ a permutation or ] was made to react, and was obtained with a corresponding sulfonic acid, Acid catalysts, such as methansulfonic acid / diphosphorus pentaoxide, or an aluminum chloride, are used for the phenyl sulfoxide which is not permuted [ a permutation or ] and a corresponding aromatic compound. Condensation, The approach of carrying out salt exchange or a diaryl iodonium salt, and a diaryl sulfide are compoundable by condensation, the approach of carrying out salt exchange, etc. using catalysts, such as copper acetate. The compound of a formula (III') is compoundable by making an aromatic compound react using a periodate. Moreover, the sulfonic acid or sulfonate used for salt exchange can be obtained by the approach of hydrolyzing commercial sulfonic-acid chloride, the approach of reacting an aromatic compound and a chlorosulfonic acid, the approach of reacting an aromatic compound and sulfamic acid, etc.

[0061] It is \*\* below about the synthetic approach of a general formula (I') – (III') concrete compound concretely. \*\*.

(Composition of a \*\* NTAFURORO benzenesulfonic acid tetramethylammonium salt) Pentough ROROPENSEN sulfonyl chloride 25g was dissolved in methanol 100m1 under ice-cooling, and 100g of tetramethylammonium hydroxide water solutions was slowly added to this 25%. When stirred at the room temperature for 3 hours, the solution of the Pentough Rollo benzenesulfonic acid tetramethylammonium salt was obtained. This solution was used for the salt exchange with sulfonium salt and iodonium salt.

[0062] (Composition of triphenylsulfonium Pentough ROROBENZEN sulfonate: Composition of an example (I-1)) The diphenyl sulfoxide 509 was dissolved in benzene 800m1, 200g of aluminum chlorides was added to this, and it flowed back for 24 hours. Water 2L was slowly filled with reaction mixture, 1 was added to this 400m of concentrated hydrochloric acid, and it heated at 70 degrees C for 10 minutes. After washing and filtering this water solution by 1 500m of ethyl acetate, what dissolved 200g of ammonium iodide in 1 400m of water was added. When ethyl acetate washed after rinsing, \*\*\*\* and, and the fine particles which deposited were dried, 70g of triphenylsulfonium iodide was obtained. Triphenylsulfonium iodide 30.5g was dissolved in

methanol 1000ml, 19.1g of silver oxides was added to this solution, and it stirred at the room temperature for 4 hours. The solution was filtered and the solution of the Pentough Rollo benzenesulfonic acid tetramethylammonium salt compounded by the above of an excessive amount to this was added. Reaction mixture was condensed, this was dissolved in dichloromethane 500ml, and a tetramethylammonium hydroxide water solution and water washed this solution 5%. When the organic phase was condensed after desiccation with anhydrous sodium sulfate, triphenylsulfonium Pentough ROROBENSEN sulfonate was obtained.

[0063] (Composition of triarylsulfonium Pentough ROROBENSEN sulfonate: Composition of an example (I-9) and the mixture of (II-1)) If triarylsulfonium chloride 50g (the product made from Fluka, triphenylsulfonium chloride 50% water solution) is dissolved in 1 500ml of water and the solution of the Pentough Rollo benzenesulfonic acid tetramethylammonium salt of an excessive amount is added to this, oil has deposited. When the oil obtained except for the supernatant was rinsed and it dried by decant, triarylsulfonium Pentough Rollo \*\* NSEN sulfonate (let an example (I-9) and (II-1) be principal components) was obtained.

[0064] (Composition of JI (4-t-amyl phenyl) iodonium Pentough ROROBENSEN sulfonate: Composition of an example (III-1)) t-amyl benzene 60g, 39.5g of potassium iodates, 81g of acetic anhydrides, and dichloromethane 170ml were mixed, and 66.8g of bottom concentrated sulfuric acid of ice-cooling was slowly dropped at this. After stirring under ice-cooling for 2 hours, it stirred at the room temperature for 10 hours. 1 was added to reaction mixture 500ml of water under ice-cooling, and when it condensed after it washed this by dichloromethane and a sodium hydrogencarbonate and water washed the extract and the organic phase, the JI (4-t-amyl phenyl) iodonium sulfate was obtained. This sulfate was added to the solution of the Pentough Rollo benzenesulfonic acid tetramethylammonium salt of an excessive amount. 1 was added to this solution 500ml of water, and when it condensed after it washed this by dichloromethane and a tetramethylammonium hydroxide water solution and water washed the extract and the organic phase 5%, JI (4-t-amyl phenyl) iodonium Pentough ROROBENSEN sulfonate was obtained. It is compoundable by using an approach with the same said of other compounds.

[0065] The component (a) used in this invention is not restricted to the compound which decomposes by the exposure of the above-mentioned electron ray or an X-ray, and generates an acid, and the well-known compounds which generate an acid by the exposure of the electron ray or X-ray currently used for the photoinitiator of optical cationic polymerization, the photoinitiator of an optical radical polymerization, the optical decolorizing agent of coloring matter, optical alterant, or a micro resist, and those mixture can be used for it, choosing them suitably.

[0066] For example S.I.Schlesinger, Photogr.Sci.Eng., 18,387 (1974), T. Diazonium salt given in S.Bal et al, Polymer, 21,423 (1980), etc., U.S. Pat. No. 4,069,055, said 4,069,056 numbers, \*\* Re No. 27,992, 17 Ammonium salt given in Japanese Patent Application No. No. 140,140 [ three to ] etc., D.C.Necker et al, Macromolecules, 2468 (1984), C. S.Wen et al, Teh, Proc.Conf.Rad.Curing ASIA, p478 Tokyo, Oct (1988), Phosphonium salt given in U.S. Pat. No. 4,069,055, said 4,069,056 numbers, etc., J. V.Crivello et al, Macromolecules, 10 (6), 1307 (1977), Chem.&Eng.News, Nov.28, p31 (1988), The Europe patent No. 104,143, U.S. Pat. No. 339,049, 410,201, Iodonium salt given in JP,2-150,848,A, JP,2-296,514,A, etc., J. -- V.Crivello et al and Polymer J. -- 17 and 73 (1985) -- J. 43 V.Crivello et al.J.Org.Chem., 3055 (1978), W. 22 R.Watt et al, J.Polymer Sci., Polymer Chem.Ed., 1789 (1984), J. V.Crivello et al, Polymer Bull., 14,279 (1985), J. V.Crivello

etal, *Macromolecules*, 14 (5), 17 1141 (1981), J.V.Crivello etal, *J.PolymerSci., Polymer Chem.Ed.*, 2877 (1979), Europe patent 370,693rd A number, said 3,902,114 numbers, said 233,567 numbers, Said 297,443 numbers, said 297,442 numbers, U.S. Pat. No. 4,933,377, said -- No. 161,811 -- said -- No. 410,201 -- said -- No. 339,049 -- said -- No. 4,760,013 said -- No. 4,734,444 -- said -- 2,833,827 A number and the Germany patent No. 2,904,626 Sulfonium salt given in said 3,604,580 numbers, said 3,604,581 numbers, etc., J. V.Crivello etal, *Macromolecules*, 10 (6), 1307 (1977), J.V.Crivello etal, *J.PolymerSci., Polymer Chem.Ed.*, 17, and 1047 (1979) etc. -- the seleno NIUMU salt of a publication -- C. -- S.Wen etal, *Teh, Proc.Conf.Rad.Curing ASIA*, p478 Tokyo, and Oct (1988) etc. -- onium salt, such as arsonium salt of a publication, -- U.S. Pat. No. 3,905,815, JP,46-4605,B, JP,48-36281,A, JP,55-32070,A, JP,60-239736,A, JP,61-169835,A, JP,61-169837,A, JP,62-58241,A, JP,62-212401,A, An organic halogenated compound given in JP,63-70243,A, JP,63-298339,A, etc., KMeier etal, *J.Rad.Curing*, 13 (4), 26 (1986), T.P.Gill 19 etal, *Inorg.Chem.*, 3007 (1980), D. Astruc, *Acc.Chem.Res.*, 19 (12), 377 (1986), An organic metal / organic halogenide given in JP,2-161445,A etc., S. Hayase etal, *J.Polymer Sci.*, 25,753 (1987), E. 23 Reichmanisetal, *J.Polymer Sci., Polymer Chem.Ed.*, 1 (1985), Q. Q.Zhu etal, *J.Photochem.*, 36, 85, 39,317 (1987), B.Amit etal, *Tetrahedron Lett.*, (24) 2205 (1973), D.H.R.Barton etal, *J.Chem Soc.*, 3571 (1965), P.M.Collins etal, *J.Chem.Soc., Perkin I*, 1695 (1975), M. Rudinstein etal, *Tetrahedron Lett.*, (17), 110 1445 (1975), J.W.Walker etal, *J.Am.Chem.Soc.*, 7170 (1988), S.C.Busman etal, *J.Imaging Technol.*, 11 (4), 21 191 (1985), H.M.Houlihan etal, *Macromolecules*, 2001 (1988), P. M.Collins etal, *J.Chem.Soc., Chem.Comm.*, 532 (1972), S. 18 Hayase etal, *Macromolecules*, 1799 (1985), E. Reichmanis etal, *J.Electrochem.Soc., Solid State Sci.Technol.*, 130 (6), 21 F.M.Houlihan etal, *Macromolecules*, 2001 (1988), the Europe patent 0290th and No. 750 -- said -- No. 046 or 083 -- said -- No. 156 or 535 said -- No. 271,851 -- said -- 0,388,343 Number, U.S. Pat. No. 3,901,710 -- The photo-oxide generating agent which has o-nitrobenzyl mold protective group of a publication in said 4,181,531 numbers, JP,60-198538,A, JP,53-133022,A, etc., M. TUNOOKA etal, *Polymer Preprints Japan*, 35 (8), G. Berner etal, *J.Rad.Curing*, 13 (4), W. J.Mijs etal, *Coating Technol.*, 55 (697) and 45 (1983), Akzo, H.Adachi etal, *Polymer Preprints, Japan*, 37 (3), the Europe patent 0199th and No. 672 -- said -- No. 84515 -- said -- No. 199 or 672 -- said -- No. 044 or 115 -- said -- No. 0101 or 122 and U.S. Pat. No. 618,564 -- said -- No. 4,371,605 -- said -- the disulfon compound of a publication can be mentioned to a compound which photodissociates and generates a sulfonic acid, JP,61-166544,A, etc. which are represented by imino sulfonate given in No. 4,431,774, JP,64-18143,A, JP,2-245756,A, Japanese Patent Application No. No. 140109 [ three to ], etc.

[0067] moreover, the radical which generates an acid by the exposure of these electron rays or an X-ray or the compound which introduced the compound into the principal chain or side chain of a polymer -- for example M. E.Woodhouse 104 etal, *J.Am.Chem.Soc.*, 5586 (1982), S. P.Pappas etal, *J.Imaging Sci.*, 30 (5), 218 (1986), S.Kondo etal, *Makromol.Chem., Rapid Commun.*, 9,625 (1988), Y. Yamada etal, *Makromol.Chem.*, and 152,153,163 (1972), J. 17 V.Crivello etal, *J.PolymerSci., Polymer Chem.Ed.*, 3845 (1979), U.S. Pat. No. 3,849,137, the Germany patent No. 3914407, JP,63-26653,A, JP,55-164824,A, JP,62-69263,A, Provisional-Publication-No. 63- The compound of a publication can be used for No. 146038, JP,63-163452,A, JP,62-153853,A, JP,63-146029,A, etc.

[0068] Furthermore, the compound which generates an acid by the light of a publication can also be used for V.N.R.Pillai, *Synthesis*, (1), 1 (1980), A.Abad etal, *Tetrahedron Lett.*, (47) 4555 (1971), D.H.R.Barton etal,

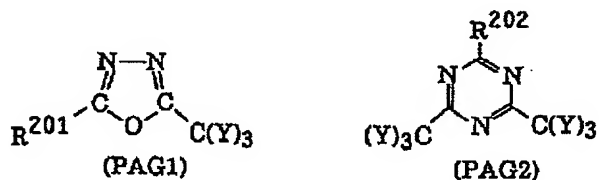
J.Chem.Soc., (C), 329 (1970), U.S. Pat. No. 3,779,778, the Europe patent No. 126,712, etc.

[0069] In the compound which decomposes by the exposure of the electron ray in which the above-mentioned concomitant use is possible, or an X-ray, and generates an acid, especially the thing used effectively is explained below.

(1) S-triazine derivative expressed with the oxazole derivative or general formula (PAG2) expressed with the following general formula (PAG1) which the trihalomethyl group permuted.

[0070]

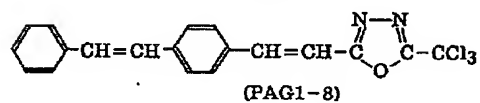
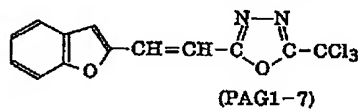
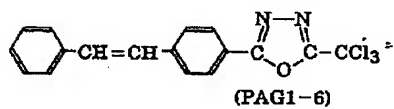
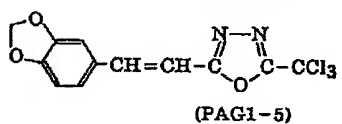
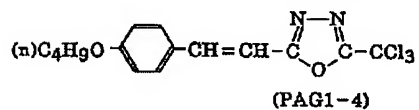
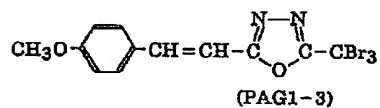
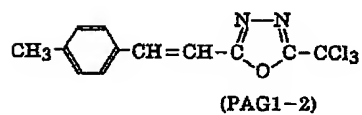
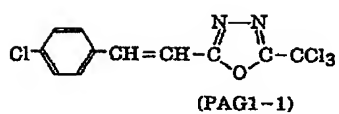
[Formula 25]



[0071] The inside of a formula, and R<sup>201</sup> The aryl group which is not permuted [ a permutation or ], an alkenyl radical, and R<sup>202</sup> The aryl group which is not permuted [ a permutation or ], an alkenyl radical, an alkyl group, and -C (Y)<sub>3</sub> are shown. Y shows a chlorine atom or a bromine atom. Although the following compounds can specifically be mentioned, it is not limited to these.

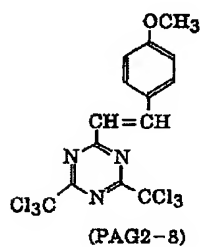
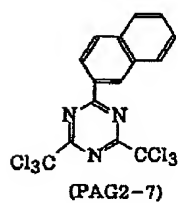
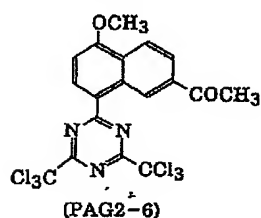
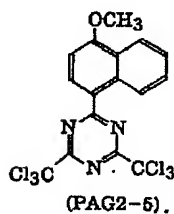
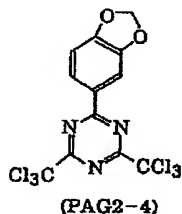
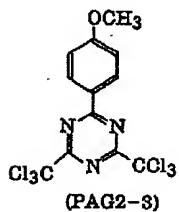
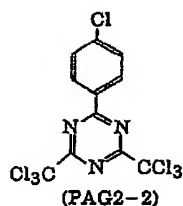
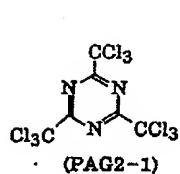
[0072]

[Formula 26]



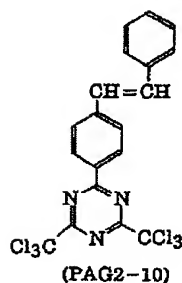
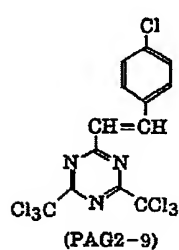
[0073]

[Formula 27]



[0074]

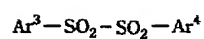
[Formula 28]



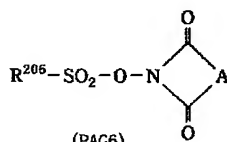
[0075] (2) The imino sulfonate derivative expressed with the disulfon derivative or general formula (PAG6) expressed with the following general formula (PAG5).

[0076]

[Formula 29]



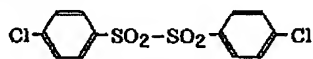
(PAG5)



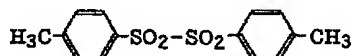
[0077] Ar3 and Ar4 show respectively the aryl group which is not permuted [ a permutation or ] independently among a formula. R206 The alkyl group which is not permuted [ a permutation or ] and an aryl group are shown. A shows the alkylene group which is not permuted [ a permutation or ], an alkenylene group, and an arylene radical. Although the compound shown below as an example is mentioned, it is not limited to these.

[0078]

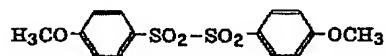
[Formula 30]



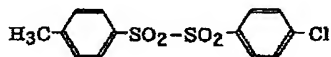
(PAG5-1)



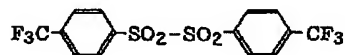
(PAG5-2)



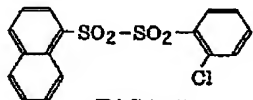
(PAG5-3)



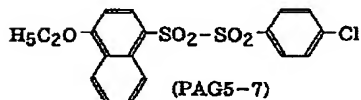
(PAG5-4)



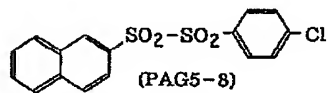
(PAG5-5)



(PAG5-6)



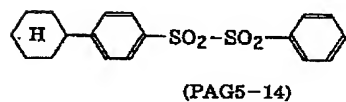
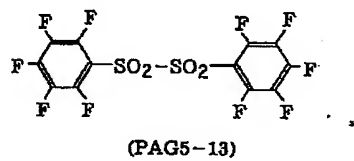
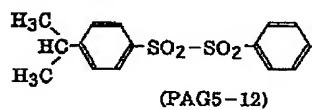
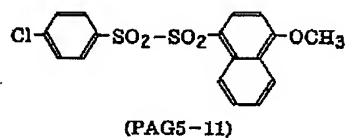
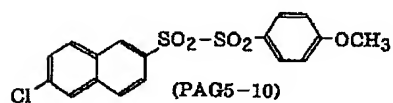
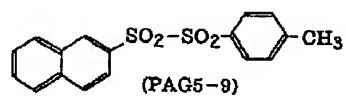
(PAG5-7)



(PAG5-8)

[0079]

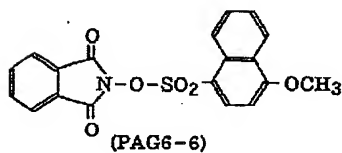
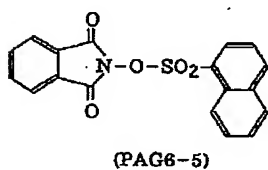
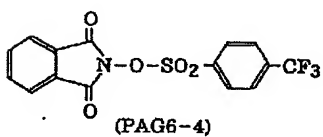
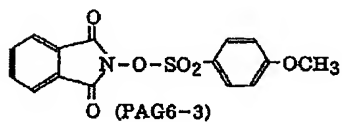
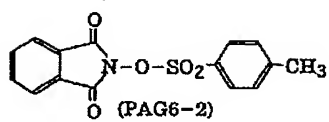
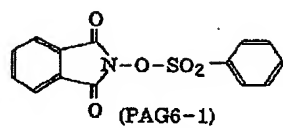
[Formula 31]



[0080]

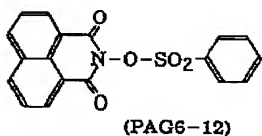
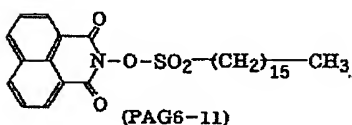
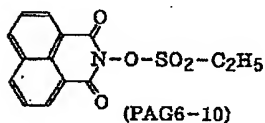
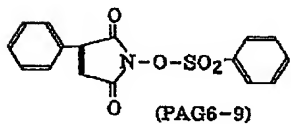
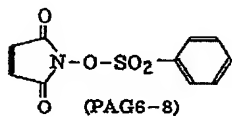
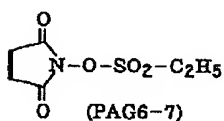
[Formula 32]





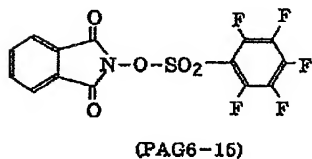
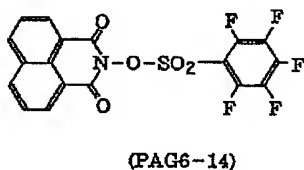
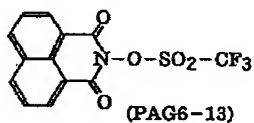
[0081]

[Formula 33]



[0082]

[Formula 34]



[0083] A component (a) may be used independently, or plurality may be mixed and used for it. The total content as that of a component (a) is 0.1 - 20 % of the weight usually 1 - 7 % of the weight still more preferably 0.5 to 10% of the weight preferably to the positive type electron ray of this invention, or the solid

content of an X ray resist constituent all constituent.

[0084] [II] The resin used by acidolysis nature resin this invention is resin which has a balking radical containing the residue of a compound which has Ip value smaller than the ionization potential (Ip) value of p-ethylphenol and to which the solubility over an alkali developer increases according to an operation of an acid. Ip value said here points out what was computed by the molecular orbital count by MOPAC. The molecular orbital count by MOPAC is James J.P.Stewart, Journal of Computer-Aided Molecular Design Vol.4, No.1 (1990), and pp.1-105. It is based on the indicated technique. This molecular orbital count is Oxford Molecular. It can carry out by using the software of a shrine, and CAChe. In addition, as a parameter used in this count, PM3 parameter is desirable. Ip value is 8.2 or less still more preferably 8.6 or less more preferably less than 8.9. Although not limited especially about a minimum, it is four or more still more preferably three or more more preferably two or more.

[0085] In this invention, the residue of a compound which has Ip value smaller than p-ethylphenol means the radical excluding one hydrogen atom from the compound which has the Ip value concerned.

[0086] As for the resin of this invention, it is desirable to have the repeat unit expressed with the above-mentioned general formula (I) as a repeat unit which has the above-mentioned balking radical. In a formula (I), a hydrogen atom or a methyl group, and R2 and R3 are [ a divalent organic radical and X of a hydrogen atom or the alkyl group of carbon numbers 1-4, and W ] organic radicals independently, respectively, and R1 has Ip value of H-O-X smaller than Ip value of p-ethylphenol. n is the integer of 0-4 and is 1 or 2 preferably. when n is plurality, even if two or more W is the same, it may differ. In addition, the radical from the carbon atom with which R2 and R3 have combined the balking radical in a formula (I) in common to X corresponds.

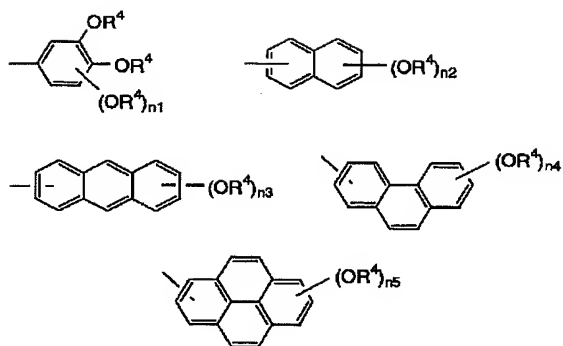
[0087] The combination of independent [ which is chosen from the group which consists of an alkylene group, a cyclo alkylene group, a ether group, a thioether radical, a carbonyl group, an ester group, an amide group, a sulfonamide radical, a urethane group, and an urea radical as a divalent organic radical of W ], or two radicals or more is expressed. The radical expressed with the following type can be mentioned as an alkylene group. - Rf and Rg express a hydrogen atom, an alkyl group, a permutation alkyl group, and an alkoxy group among the [C (Rf) and (Rg)] r-above-mentioned type, and even if both are the same, they may differ. As an alkyl group, low-grade alkyl groups, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, and butyl, are chosen from a methyl group, an ethyl group, a propyl group, and an isopropyl group desirable still more preferably. An alkoxy group etc. can be mentioned as a substituent of a permutation alkyl group. As an alkoxy group, the thing of the carbon numbers 1-4, such as a methoxy group, an ethoxy radical, a propoxy group, and a butoxy radical, can be mentioned. r is the integer of 1-10. As a cyclo alkylene group, ten things are mentioned from a carbon number 3, and a cyclo pentene radical, a cyclo hexylene radical, a cyclo octylene radical, etc. can be mentioned.

[0088] As for the alkyl group of the carbon numbers 1-4 as R2 and R3, a methyl group, an ethyl group, a propyl group, n-butyl, iso-butyl, s-butyl, t-butyl, etc. are mentioned.

[0089] Moreover, it is desirable that it is the structure where X in a formula (I) is expressed with a formula (II).  
-L-Y (II)

For the inside of a formula (II), and L, single bond or an alkylene group, and Y are [0090].

[Formula 35]



[0091] since — the radical chosen is expressed. Here,  $R^4$  expresses the straight chain of carbon numbers 1–6, or the alkyl group of branching. The radical expressed with the following type can be mentioned as an alkylene group as L.

–  $R_f$  and  $R_g$  express a hydrogen atom, an alkyl group, a permutation alkyl group, and an alkoxy group among the  $[C(R_f) \text{ and } (R_g)]$  r–above–mentioned type, and even if both are the same, they may differ. As an alkyl group, the alkyl group of the carbon numbers 1–4, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, and butyl, is chosen from a methyl group, an ethyl group, a propyl group, and an isopropyl group desirable still more preferably. As a substituent of a permutation alkyl group, an alkoxy group (preferably carbon numbers 1–4) can be mentioned. As an alkoxy group, the thing of the carbon numbers 1–4, such as a methoxy group, an ethoxy radical, a propoxy group, and a butoxy radical, can be mentioned. r is the integer of 1–10.

[0092] A methyl group, an ethyl group, a propyl group, butyl, a pentyl radical, a hexyl group, etc. are mentioned, and the straight chain of the carbon numbers 1–6 as  $R^4$  or the alkyl group of branching may have the substituent. As a substituent, as a substituent, a halogen atom, an alkoxy group, an alkoxy carbonyl group, an acyl group, an acyloxy radical, etc. are mentioned, and it is ten or less carbon number preferably.

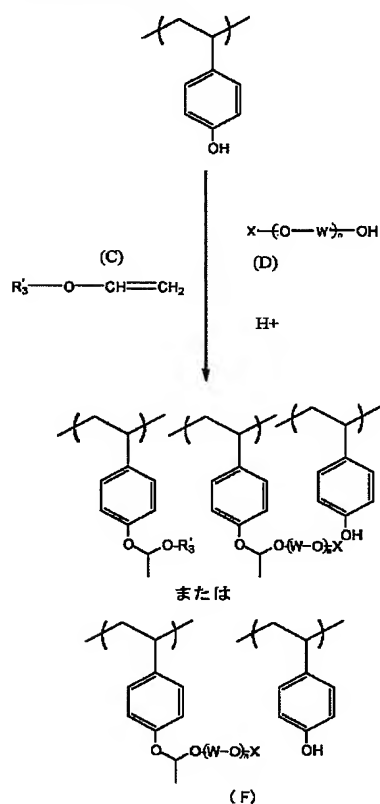
[0093] The compound which has at least one addition polymerization nature unsaturated bond chosen as a monomer of the repeat unit which gives the balking radical of this invention from the permutation styrene represented by p-hydroxystyrene, m-hydroxystyrene, a vinyl benzoic acid, the styrene sulfonic acid, etc., acrylic ester (meta), an acrylic-acid (meta) amide, a maleic anhydride, fumaric-acid ester, maleimide, an allyl compound, vinyl ether, and vinyl ester is mentioned.

[0094] Or (b2) is used by this invention (b1), and a polymer can be obtained by carrying out the acetalization reaction of a part of the phenolic hydroxyl group of the trunk polymer which has a phenolic hydroxyl group using the corresponding vinyl ether compound and acid catalyst. For example, an acetal radical can be introduced into JP,5-249682,A, JP,8-123032,A, and JP,10-221854,A by the approach of a publication. Moreover, or (b2) is used by this invention (b1), and a polymer is J.Photopolym.Sci.Tech. and 11 (3). It was indicated by 431 (1998). S. It is possible to introduce a desired acetal radical using the acetal exchange reaction of Malik. That is, or (b2) is used by this invention (b1), and, as for a polymer, it is desirable that it is resin which the alcoholic compound expressed with the vinyl ether compound and the above–mentioned general formula (D) which are expressed with the alkali fusibility polymer which has a hydroxyl group, and the above–mentioned general formula (C) is made to react under an acid catalyst, and is obtained. Here, as an alkali fusibility polymer which has a hydroxyl group, the resin which has a phenolic hydroxyl group is desirable,

and is polyhydroxy styrene or a polyhydroxy styrene copolymer more preferably. Here, as an acid catalyst, p-toluenesulfonic acid, p-toluenesulfonic-acid pyridinium salt, etc. can be used. As shown for example, in the following reaction formula, this approach can introduce only R3 and R4, or R4 as an acetal radical by making the resin which has a phenolic hydroxyl group, and the alcoholic compound shown by the vinyl ether compound shown by the above-mentioned general formula (C), and the above-mentioned general formula (D) react under acid-catalyst existence, as shown in the following general formula (F).

[0095]

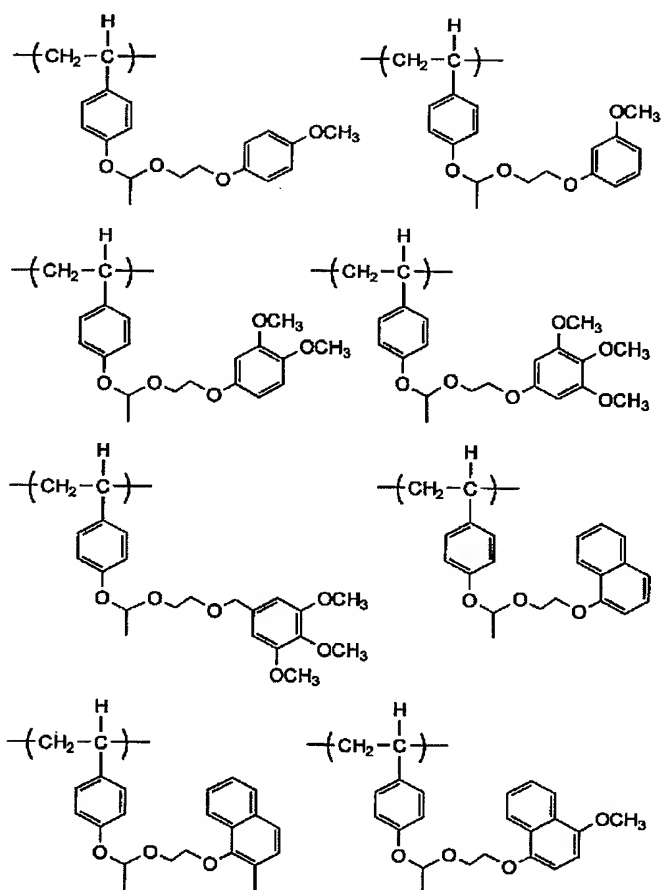
[Formula 36]



[0096] without it compounds a reaction precursor (vinyl ether) as the approach of acetalization in this invention — acquisition — the acetal exchange reaction which can be performed using easy alcohol is desirable. Although the example of a repeat unit of having the balking radical used for below by this invention is given, it is not limited to these.

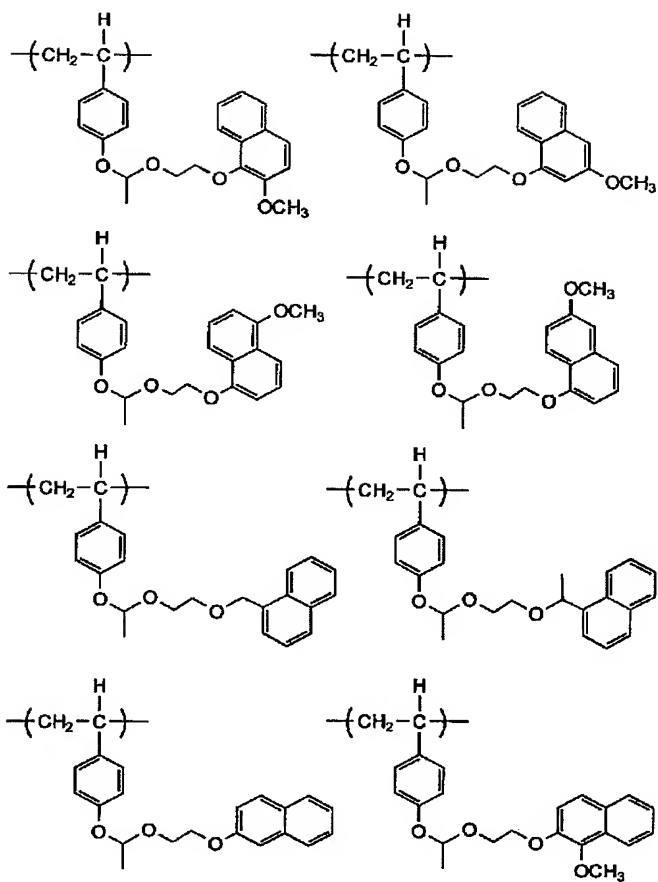
[0097]

[Formula 37]



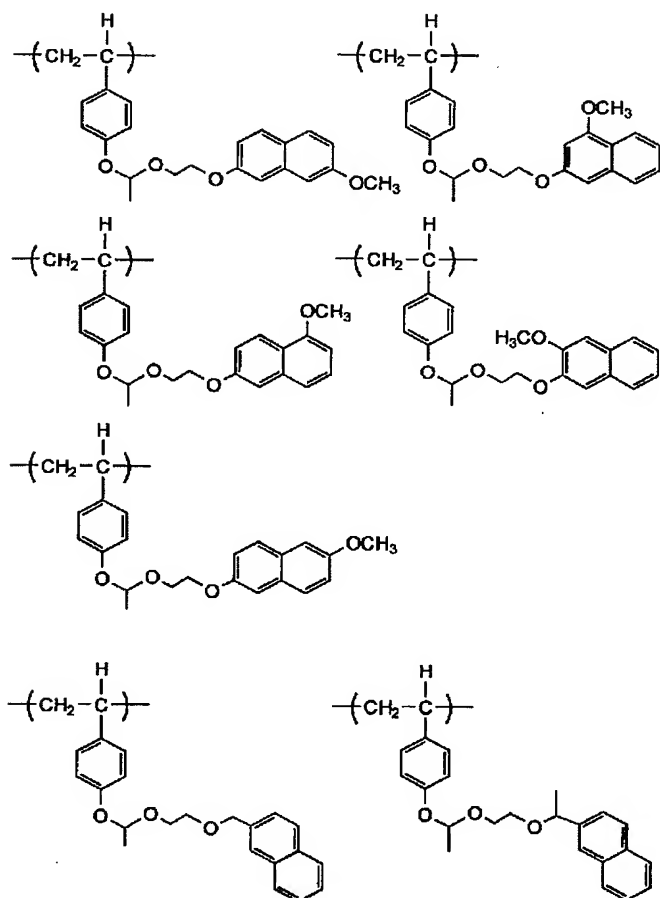
[0098]

[Formula 38]



[0099]

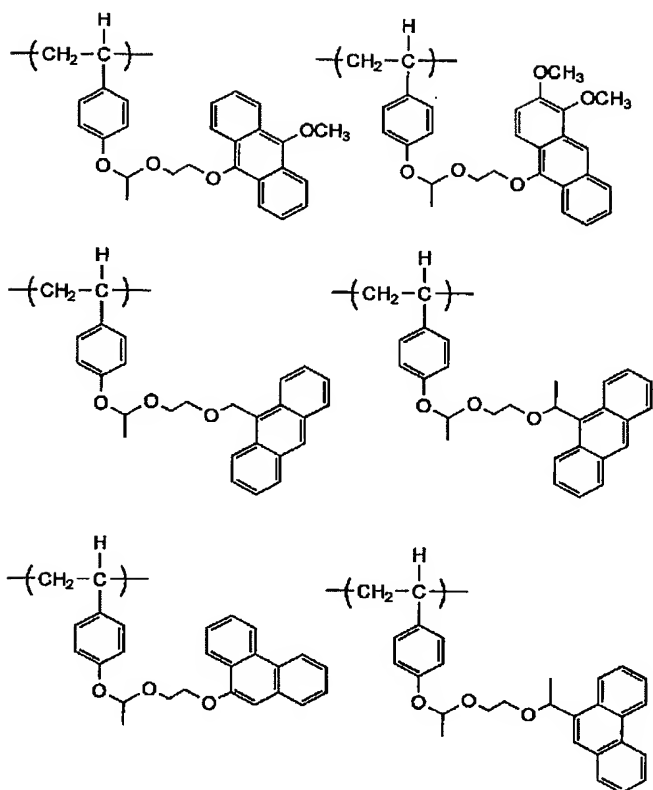
[Formula 39]



[0100]

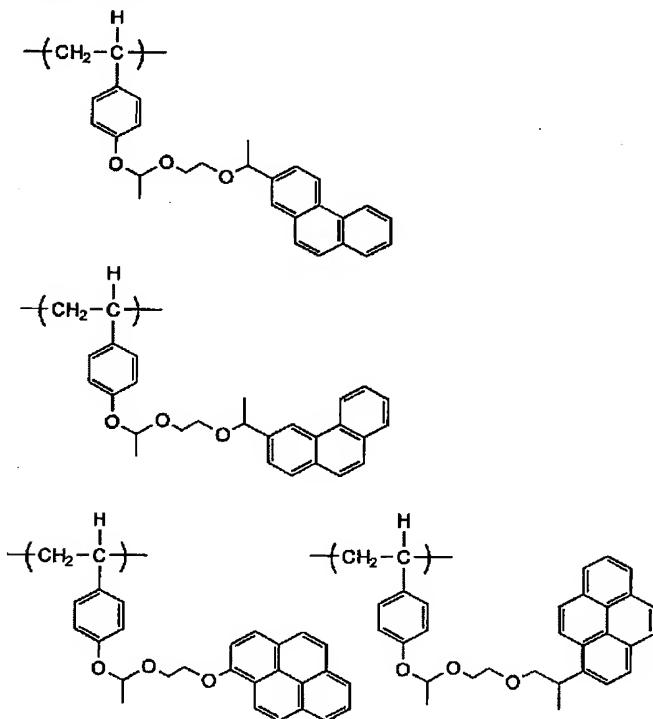
[Formula 40]





[0101]

[Formula 41]



[0102] The acidolysis nature resin in this invention is compoundable by carrying out a polymerization the monomer of the repeat unit which has the specific balking radical of this invention, and if needed with the

monomer of the repeat unit which has other leaving groups (acidolysis nature machine), and the monomer which does not have an acidolysis nature machine.

[0103] That is, further, various repeat structural units can be contained in order to adjust dry etching resistance, standard developer fitness and substrate adhesion, a resist profile, the resolution that is the general required property of a resist, thermal resistance, sensibility, etc.

[0104] Although the repeat structural unit equivalent to the following monomer can be mentioned as such a repeat structural unit, it is not limited to these. Thereby, fine tuning of the adhesion to the substrate of the engine performance required of acidolysis nature resin, the solubility over (1) spreading solvent, (2) film-production nature (glass transition point), (3) alkali development property, (4) \*\*\*\*\* (relative-degree-of-intimacy aqueousity, alkali fusibility radical selection), and (5) unexposed parts, (6) dry-etching resistance, etc. is attained especially.

[0105] The compound which has one addition polymerization nature unsaturated bond chosen from for example, acrylic ester, methacrylic ester, acrylamides, methacrylamide, an allyl compound, vinyl ether, and vinyl ester as such a monomer can be mentioned.

[0106] Specifically, the following monomers can be mentioned. Acrylic ester (the carbon number of an alkyl group is alkyl acrylate of 1-10 preferably) : A methyl acrylate, An ethyl acrylate, acrylic-acid propyl, acrylic-acid amyl, acrylic-acid cyclohexyl, Acrylic-acid ethylhexyl, acrylic-acid octyl, acrylic-acid-t-octyl, Chlorethyl acrylate, 2-hydroxyethyl acrylate 2, 2-dimethyl hydroxypropyl acrylate, 5-hydroxy pentyl acrylate, trimethylol propane monoacrylate, pentaerythritol monoacrylate, benzyl acrylate, methoxybenzyl acrylate, furfuryl acrylate, tetrahydrofurfuryl acrylate, etc.

[0107] Methacrylic ester (the carbon number of an alkyl group is alkylmetaacrylate of 1-10 preferably) : Methyl methacrylate, Ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, Amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, Benzyl methacrylate, KURORU benzyl methacrylate, octyl methacrylate, 2-hydroxyethyl methacrylate, 4-hydroxy butyl methacrylate, 5-hydroxy pentyl methacrylate, 2, and 2-dimethyl-3-hydroxypropyl methacrylate, Trimethylol propane mono-methacrylate, pentaerythritol mono-methacrylate, furfuryl methacrylate, tetrahydrofurfuryl methacrylate, etc.

[0108] Acrylamides: Acrylamide, N-alkyl acrylamide (carbon numbers 1-10 as an alkyl group) for example, there are a methyl group, an ethyl group, a propyl group, butyl, t-butyl, a heptyl radical, an octyl radical, a cyclohexyl radical, a hydroxyethyl radical, etc. N and N-dialkyl acrylamide (carbon numbers 1-10 as an alkyl group) For example, N-hydroxyethyl-N-methylacrylamide, N-2-acetamidoethyl-N-acetyl acrylamide, etc. with a methyl group, an ethyl group, butyl, an isobutyl radical, an ethylhexyl radical, a cyclohexyl radical, etc.

[0109] Methacrylamide: Methacrylamide, N-alkyl methacrylamide (as alkyl group, there are thing of carbon numbers 1-10, for example, methyl group, ethyl group, t-butyl, ethylhexyl radical, hydroxyethyl radical, cyclohexyl radical, etc.), N, and N-dialkyl methacrylamide (there are an ethyl group, a propyl group, butyl, etc. as an alkyl group), N-hydroxyethyl-N-methyl methacrylamide, etc.

[0110] Allyl compound: Allyl ester, allyloxy ethanol (for example, an acetic-acid allyl compound, allyl caproate, a caprylic-acid allyl compound, a lauric-acid allyl compound, a palmitic-acid allyl compound, a stearic acid allyl compound, allyl benzoate, an acetoacetic-acid allyl compound, a lactic-acid allyl compound, etc.), etc.

[0111] vinyl ether: -- alkyl vinyl ether (for example, hexyl vinyl ether --) Octyl vinyl ether, DESHIRU vinyl ether, ethylhexyl vinyl ether, Methoxy ethyl vinyl ether, ethoxyethyl vinyl ether, KURORU ethyl vinyl ether,

The 1-methyl -2, 2-dimethyl propyl vinyl ether, 2-ethyl butyl vinyl ether, Hydroxyethyl vinyl ether, diethylene-glycol vinyl ether, dimethylaminoethyl vinyl ether, diethylamino ethyl vinyl ether, butylamino ethyl vinyl ether, benzyl vinyl ether, tetrahydrofurfuryl vinyl ether, etc.

[0112] Vinyl ester: Vinyl butyrate, vinyl iso butyrate, vinyl trimethyl acetate, vinyl diethyl acetate, vinyl BARETO, vinyl caproate, vinyl KURORU acetate, vinyl dichloro acetate, vinyl methoxy acetate, vinyl butoxy acetate, vinyl acetoacetate, vinyl lactate, vinyl-beta-phenyl butyrate, vinyl cyclohexyl carboxylate, etc.

[0113] Itaconic-acid dialkyls: Dimethyl itaconate, itaconic-acid diethyl, dibutyl itaconate, etc. The dialkyl ester or monoalkyl ester of boletic acid; dibutylfumarate etc.

[0114] In addition, a crotonic acid, an itaconic acid, acrylonitrile, a methacrylonitrile, MAREIRO nitril, etc.

[0115] In addition, copolymerization may be carried out as long as it is the unsaturated compound of the monomer equivalent to the above-mentioned various repeat structural units, and copolymerizable addition polymerization nature.

[0116] In acidolysis nature resin, further, the content mole ratio of each repeat structural unit is suitably set up, in order to adjust the dry etching resistance of a resist, standard developer fitness and substrate adhesion, a resist profile, the resolution that is the general requirement of a resist, thermal resistance, sensibility, etc.

[0117] The acidolysis nature resin in this invention is compoundable by well-known approaches, such as a radical polymerization, cationic polymerization, and anionic polymerization. Although it is simplest to perform a radical polymerization combining a corresponding monomer, when cationic polymerization and anionic polymerization are used depending on a monomer, it can compound more suitably. Moreover, when a monomer causes reactions other than a polymerization with a polymerization initiation kind, the polymer desired by carrying out the polymerization of the monomer which introduced the suitable protective group, and carrying out deprotection after a polymerization can be obtained. The polymerization method is indicated by experimental science lecture 28 macromolecule composition, new experimental science lecture 19 polymer chemistry [I], etc.

[0118] the content of the monomer of the repeat unit which has the balking radical of this invention in acidolysis nature resin -- all repeat units -- receiving -- general -- 5-40-mol % -- it is 10-25-mol % preferably.

[0119] Moreover, molecular weight exceeds 3,000 and the acidolysis nature resin of this invention is 1,000,000 or less. Preferably, weight average molecular weight exceeds 3,000 and is 500,000 or less. More preferably, weight average molecular weight exceeds 3,000 and is 100,000 or less.

[0120] As for the molecular weight distribution ( $M_w/M_n$ ) of acidolysis nature resin compoundable by the above-mentioned synthetic approach, it is desirable that it is 1.0-1.5, and, thereby, especially a resist can be high-sensitivity-ized. In addition, the resin of such a molecular weight distribution is compoundable by using living anionic polymerization in the above-mentioned synthetic approach.

[0121] (c) Acetal compound.

The (c) component in this invention is a compound expressed with a general formula (A) and/or a general formula (B).  $R_1'$  and  $R_2'$  express independently the organic radical of 1-30 carbon numbers, respectively. As a carbon number of this organic radical, it is 2-20 pieces preferably, and they are 4-16 pieces more preferably. As an organic radical of 1-30 carbon numbers of  $R_1'$  and  $R_2'$ , a straight line, branching or the alkyl

group that may have the annular substituent, the aryl group which may have the substituent, or the aralkyl radical which may have the substituent is mentioned.

[0122] As a straight chain, branching, or an annular alkyl group, the alkyl group of 1–12 carbon numbers, such as a methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl, sec-butyl, t-butyl, a hexyl group, a 2-ethylhexyl radical, an octyl radical, a cyclo propyl group, a cyclopentyl group, a cyclohexyl radical, and 1-adamantyl ethyl group, is raised. As further substituent of these alkyl groups, halogen atoms, such as a hydroxyl group, a fluorine, chlorine, a bromine, and iodine, the amino group, a nitro group, a cyano group, a carbonyl group, an ester group, an alkoxy group, the cycloalkyl radical that may contain the hetero atom, an aryloxy group, the substituent which has a sulfonyl group are mentioned. As a carbonyl group, an alkylation carbonyl group and an aromatic substitution carbonyl group are desirable, an alkylation ester group and an aromatic substitution ester group are desirable as an ester group here, and a methoxy group, an ethoxy radical, a propoxy group, a t-butoxy radical, etc. are desirable as an alkoxy group. As a cycloalkyl radical, a cyclohexyl radical, an adamantyl radical, a cyclopentyl group, a cyclo propyl group, etc. are mentioned, for example, and an oxo-RANIRU radical etc. is mentioned as a thing containing a hetero atom. As an aryloxy group, a phenoxy group etc. is mentioned and you may have the substituent in this aryl group. As a substituent which has a sulfonyl group, aryl sulfonyl groups, such as alkyl sulfonyl groups, such as a methylsulfonyl radical and an ethyl sulfonyl group, and a phenyl sulfonyl group, etc. are mentioned.

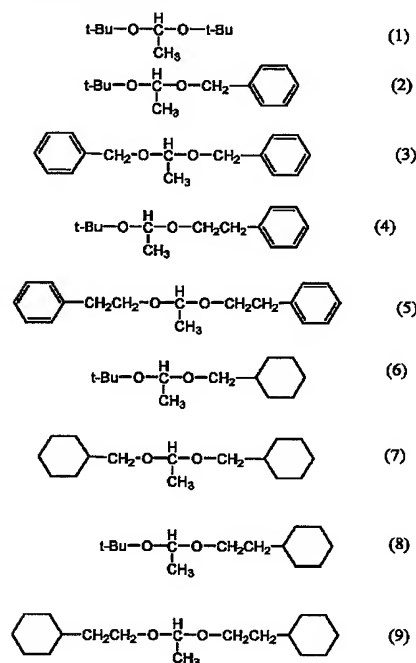
[0123] As an aryl group, benzene, naphthalene, a phenanthrene, an anthracene, a pyrene frame, etc. are mentioned as a frame of a ring, the thing of 6–30 carbon numbers is specifically mentioned, and a phenyl group, a naphthyl group, a phenan TORENIRU radical, an anthracenyl group, etc. are mentioned. In these aryl groups, it can have as a substituent what was indicated by the further substituent of an alkyl group. As an aralkyl radical, benzene, naphthalene, a phenanthrene, an anthracene, a pyrene frame, etc. are mentioned as a frame of a ring, the thing of 7–30 carbon numbers is specifically mentioned, and benzyl, a phenethyl radical, a benzhydryl group, a naphthyl methyl group, etc. are raised. On these aralkyl radicals, it can have as a substituent what was indicated by the further substituent of an alkyl group. As an organic radical of 1–30 carbon numbers of R1' and R2' Preferably A methyl group, an ethyl group, n-propyl group, i-propyl group, n-butyl, i-butyl, t-butyl, n-pentyl radical, n-hexyl group, A cyclohexyl radical, a cyclohexyl ethyl group, a phenyl group, a phenylmethyl radical, A phenylethyl radical, 3, 4-dimethoxy phenyl group, 3 and 4, 5-trimethoxyphenyl radical, 3, 4-dimethoxy phenylmethyl radical, 3 and 4, a 5-trimethoxy phenylmethyl radical, They are 1-naphthyl group, 2-naphthyl group, a 4-methoxy-1-naphthyl group, 2-(1-naphthyl) ethyl group, 9-anthryl methyl group, a 10-methoxy-1-anthryl radical, 9-phenanthrene radical, and 1-pyrenyl methyl group.

[0124] As a synthesis method of the above-mentioned acetal compound, a vinyl ether compound and an alcoholic corresponding compound can be dissolved in a suitable solvent, and it can compound by making it react under acid-catalyst existence. As an acid catalyst, p-toluenesulfonic acid, p-toluenesulfonic-acid pyridinium salt, etc. can be used here. Although it may be accompanied by acetal exchange reaction and may be obtained as mixture of two or more acetal compounds, even if a reaction is a simple substance or mixture, it can be used suitable for the purpose of this invention. As a vinyl ether compound and an alcoholic compound, it can express with the above-mentioned general formula (C) and a general formula (D) respectively. a general formula  $--(--C--)--$  setting  $--R--$  three  $--'$  -- a carbon number  $--one-30--$

a piece -- organic -- a radical -- \*\*\*\*\* -- a general formula -- (--- A ---) -- or -- a general formula -- (--- B ---) -- R -- one -- ' -- and -- R -- two -- ' -- a carbon number -- one - 30 -- a piece -- organic -- a radical -- the same -- a thing -- it can mention . Moreover, as W, X, and n in a general formula (D), it is the above-mentioned (b1), or (b2) synonymous with what resin explained by the way. The example of (c) acetal compound used suitable for this invention hereafter is shown. In addition, in the following examples, in Me, a methyl group and t-Bu express t-butyl and iso-Bu expresses an isobutyl radical.

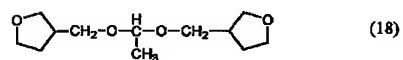
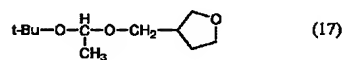
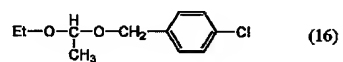
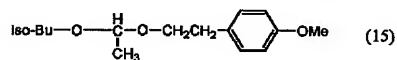
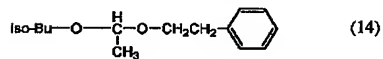
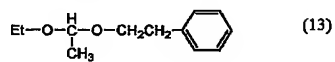
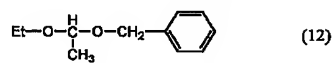
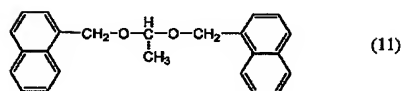
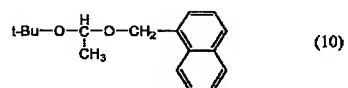
[0125]

[Formula 42]



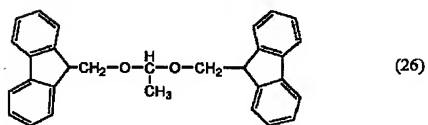
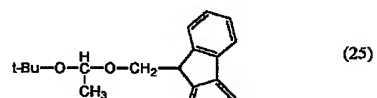
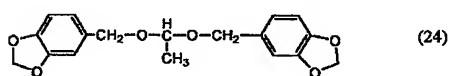
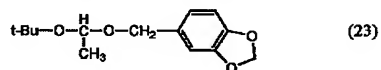
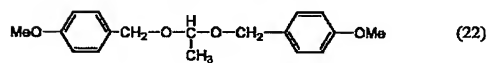
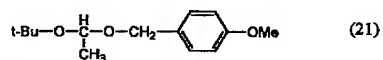
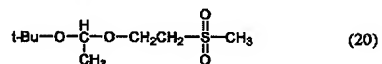
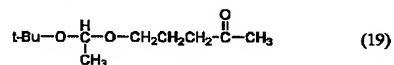
[0126]

[Formula 43]



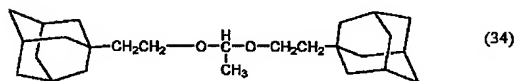
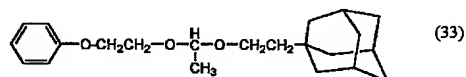
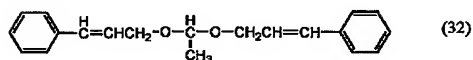
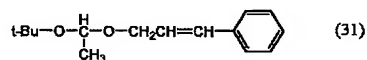
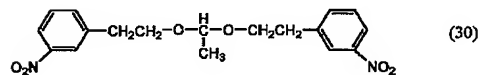
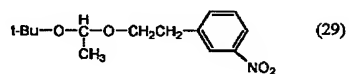
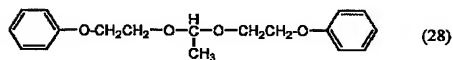
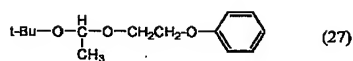
[0127]

[Formula 44]



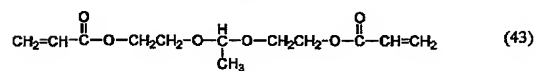
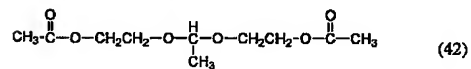
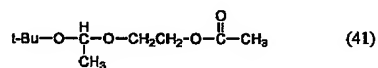
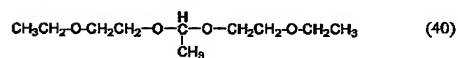
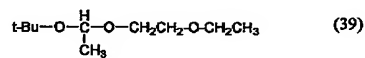
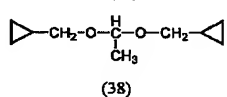
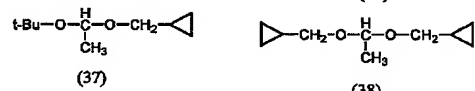
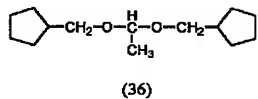
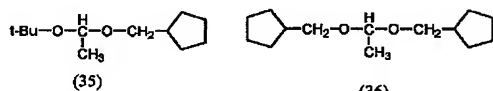
[0128]

[Formula 45]



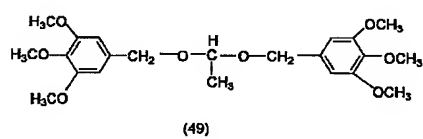
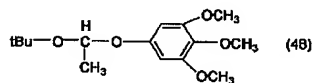
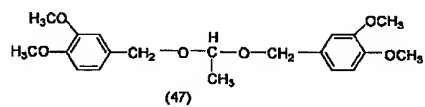
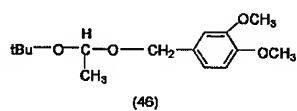
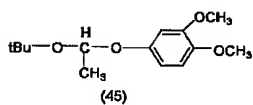
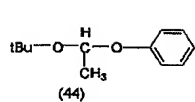
[0129]

[Formula 46]



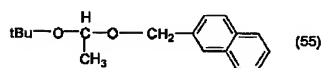
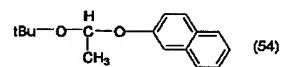
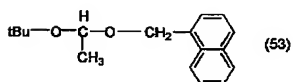
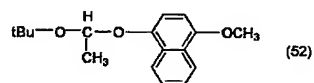
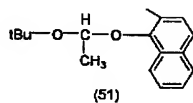
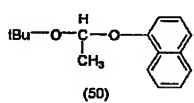
[0130]

[Formula 47]



[0131]

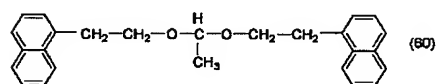
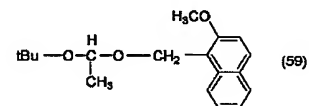
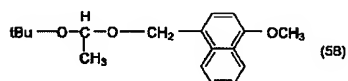
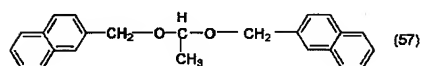
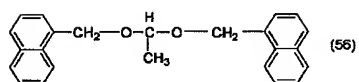
[Formula 48]



[0132]

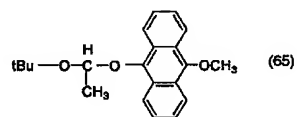
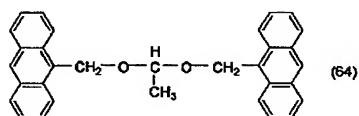
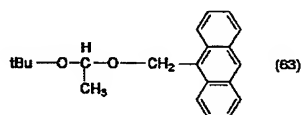
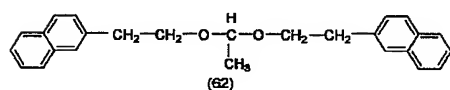
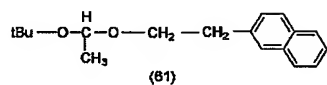
[Formula 49]





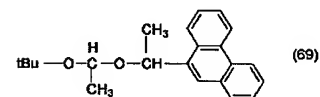
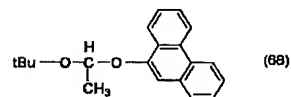
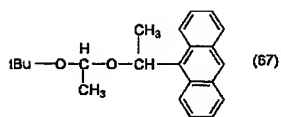
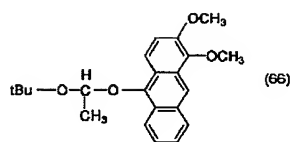
[0133]

[Formula 50]



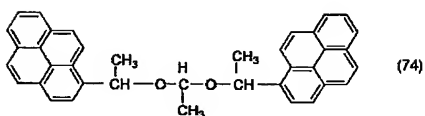
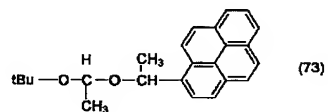
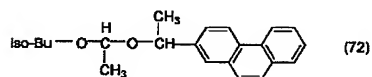
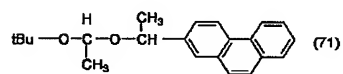
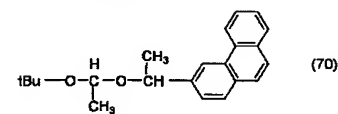
[0134]

[Formula 51]



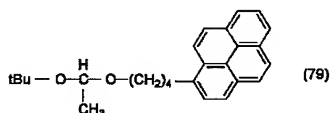
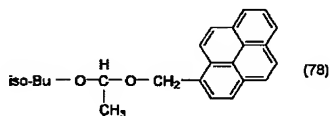
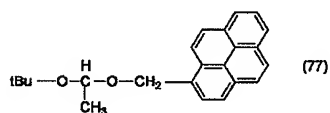
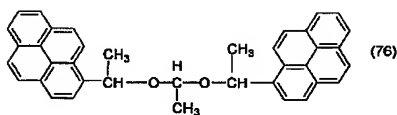
[0135]

[Formula 52]



[0136]

[Formula 53]



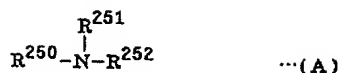
[0137] (c) acetal compound which is the indispensable component of this invention — as for or (b1) (b2), it is desirable that they are under the 100 weight sections more than the 0.1 weight section to the solid content 100 weight section of a polymer. Furthermore, it is under 50 weight sections more than 1 weight section, and they are under 30 weight sections more than 2 weight sections more preferably. Since it will become the inclination for the thermal resistance of a resist to fall if the 100 weight sections are exceeded, it may not be desirable, and effectiveness of this invention may be unable to be discovered under in the 0.1 weight section.

[0138] [III] The constituent of solvent this invention contains a solvent at the point which melts to the solvent which dissolves each above-mentioned component, and is applied on a base material. As a solvent used here, ethylene dichloride, a cyclohexanone, Cyclopentanone, 2-heptanone, gamma-butyrolactone, a methyl ethyl ketone, Ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, 2-methoxy ethyl acetate, ethylene glycol monoethyl ether acetate, Propylene glycol monomethyl ether, propylene-glycol-monomethyl-ether acetate, Propylene-glycol-monomethyl-ether propionate, toluene, Ethyl acetate, methyl lactate, ethyl lactate, methoxy methyl propionate, Ethoxy ethyl propionate, methyl pyruvate, pyruvic-acid ethyl, pyruvic-acid propyl, N.N-dimethylformamide, dimethyl sulfoxide, N-methyl pyrrolidone, a tetrahydrofuran, etc. are desirable, and independent in these solvents — or it can be mixed and used. In this invention, especially as a solvent, propylene-glycol-monomethyl-ether acetate is desirable, and, thereby, excellent in the homogeneity within a field. [ come ] The concentration of the solid content (other additives explained below are included) of the constituent of this invention makes it dissolve in a solvent 0.5 to 20% of the weight, generally, so that it may become 3 – 15 % of the weight preferably.

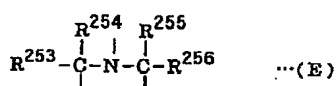
[0139] [IV] The organic base nature compound used by organic base nature compound this invention is a compound with basicity stronger than a phenol. A nitrogen-containing basicity compound is desirable especially. A nitrogen-containing basicity compound including the structure shown by following type (A) – (E) especially is desirable.

[0140]

[Formula 54]



ここで、 $\text{R}^{250}$ 、 $\text{R}^{251}$ および $\text{R}^{252}$ は、同一または異なり、水素原子、炭素数1~6のアルキル基、炭素数1~6のアミノアルキル基、炭素数1~6のヒドロキシアルキル基または炭素数6~20の置換もしくは非置換のアリール基であり、ここで $\text{R}^{251}$ と $\text{R}^{252}$ は互いに結合して環を形成してもよい。



(式中、 $\text{R}^{253}$ 、 $\text{R}^{254}$ 、 $\text{R}^{255}$ および $\text{R}^{256}$ は、同一または異なり、炭素数1~6のアルキル基を示す)

[0141] Furthermore, a desirable compound is a nitrogen-containing basicity compound which has two or more nitrogen atoms of different chemical environment in a monad, and is a compound which has especially a compound or alkylamino radical including both ring structures containing the amino group and nitrogen atom which are not permuted [ a permutation or ] preferably. As a desirable example, the aminopyridine which is not permuted [ the guanidine which is not permuted / a permutation or / a permutation, or ], The amino pyrrolidine which is not permuted [ the amino alkyl pyridine which is not permuted / a permutation or / a permutation, or ], The pyrazole which is not permuted [ in DAZORU which is not permuted / a permutation or /, a permutation or ], The pyrimidine which is not permuted [ the pyrazine which is not permuted / a permutation or /, a permutation, or ], The amino alkyl morpholine which is not permuted [ the amino morpholine which is not permuted / the piperazine which is not permuted / the pyrazoline which is not permuted / the imidazoline which is not permuted / the pudding which is not permuted / a permutation or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or ] is mentioned. Desirable substituents are the amino group, an amino alkyl group, an alkylamino radical, an amino aryl group, an arylamino radical, an alkyl group, an alkoxy group, an acyl group, an acyloxy radical, an aryl group, an aryloxy group, a nitro group, a hydroxyl group, and a cyano group.

[0142] As a desirable compound, especially Guanidine, 1, and 1-dimethyl guanidine, 1, 1, 3, 3, - tetramethyl guanidine, an imidazole, 2-methylimidazole, 4-methyl imidazole, N-methyl imidazole, 2-phenylimidazole, 4, 5-diphenyl imidazole, 2 and 4, 5-triphenyl imidazole, 2-aminopyridine, 3-aminopyridine, 4-aminopyridine, 2-dimethylamino pyridine, 4-dimethylaminopyridine, 2-diethylamino pyridine, 2-(aminomethyl) pyridine, 2-amino-3-methylpyridine, 2-amino-4-methylpyridine, 2-amino-5-methylpyridine, 2-amino-6-methylpyridine, 3-aminoethyl pyridine, 4-aminoethyl pyridine, 3-amino pyrrolidine, A piperazine, N-(2-aminoethyl) piperazine, N-(2-aminoethyl) piperidine, 4-amino - 2, 2, 6, and 6-tetramethylpiperidine, 4-piperidino piperidine, A 2-imino piperidine, 1-(2-aminoethyl) pyrrolidine, a pyrazole, 3-amino-5-methyl

pyrazole, 5 - Amino-3-methyl-1-p-tolyl pyrazole, Pyrazine, 2-(aminomethyl)-5-methyl pyrazine, a pyrimidine, 2, 4-diamino pyrimidine, 4, 6-dihydroxy pyrimidine, 2-pyrazoline, Although 3-pyrazoline, N-amino morpholine, N-(2-aminoethyl) morpholine, diazabicyclo nonene, diazabicycloundecen, etc. are mentioned, it is not limited to this.

[0143] these organic base nature compounds are independent -- it is -- two or more sorts can be combined and it can use. the compound to which the amount of the organic base nature compound used generates an acid by the exposure of the (a) electron ray of this invention, or an X-ray -- receiving -- usually -- 0.01 - ten-mol % -- it is 0.1 - five-mol % preferably. Less than [ 0.01 mol % ], the effectiveness of the addition is not acquired. On the other hand, when ten-mol % is exceeded, there is an inclination for the development nature of the fall of sensibility or a non-exposed area to get worse.

[0144] [V] A fluorine system and/or a silicon system surface active agent are used suitably, and the surface active agent which can be used for the positive type photoresist constituent of a fluorine system and/or silicon system surface-active-agent this invention can contain either of the surface active agents containing both a fluorochemical surfactant, a silicon system surface active agent and a fluorine atom, and a silicon atom, or two sorts or more. as these surfactants -- for example, JP,62-36663,A, 61-226746, 61-226745, 62-170950, 63-34540, JP,7-230165,A, 8-62834, 9-54432, 9-5988, and a U.S. Pat. No. 5405720 number -- said -- No. 5360692 -- said -- No. 5529881 -- said -- No. 5296330 -- said -- No. 5436098 -- said -- No. 5576143 -- said -- a surfactant No. 5294511 and given [ this ] in No. 5824451 can be mentioned, and the surfactant of the following marketing can also be used as it is. As a surfactant of marketing which can be used, for example, EFUTOPPU EF301 and EF303, (made in new Akita Chemicals), Fluorad 430 and FC 431 (Sumitomo 3M make), the megger fucks F171, F173, F176, F189, and R08 (Dainippon Ink make), A fluorochemical surfactant or silicon system surfactants, such as Sir chlorofluocarbon S-382, SCs 101, 102, 103, 104, 105, and 106 (Asahi Glass Co., Ltd. make), and Troysol S-366 (made in Troy Chemical), can be mentioned. Moreover, polysiloxane polymer KP-341 (Shin-Etsu Chemical Co., Ltd. make) can be used as a silicon system surfactant.

[0145] Surfactants other than a fluorine system and/or a silicon system surfactant can also be used together. Specifically The polyoxyethylene lauryl ether, polyoxyethylene stearylether, Polyoxyethylene alkyl ether, such as the polyoxyethylene cetyl ether and the polyoxyethylene oleyl ether Polyoxyethylene alkyl aryl ether, such as the polyoxyethylene octyl phenol ether and the polyoxyethylene nonyl phenol ether Polyoxyethylene polyoxypropylene block copolymers Sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, Sorbitan fatty acid esters, such as sorbitan monooleate, sorbitan trioleate, and sorbitan tristearate Polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, Polyoxyethylenesorbitan monostearate, polyoxyethylene sorbitan trioleate, The Nonion system surfactants, such as polyoxyethylene sorbitan fatty acid ester, such as polyoxyethylene sorbitan tristearate, An acrylic-acid system or methacrylic-acid system (\*\*) polymerization poly flow No.75, No.95 (product made from Kyoeisha Fats-and-oils Chemical industry), etc. can be mentioned.

[0146] The loadings of these surfactants are usually 1 or less % of the weight preferably 2 or less % of the weight to the solid content of all the constituents in the constituent of this invention. You may add independently and these surfactants can also be added combining two or more sorts.

[0147] In addition to engine performance, such as high resolution of an essential resist, pursuit of the further

advance of a semi-conductor demands the constituent of high performance from various viewpoints, such as sensibility, spreading nature, the minimum spreading initial complement, adhesion with a substrate, thermal resistance, and the preservation stability of a constituent. Recently, in order to increase the absolute magnitude which can take the chip of completion, it is in the inclination which creates a device using Wafer of the diameter of macrostomia. However, if it applies to the diameter of macrostomia, in order to be anxious about the fall of thickness homogeneity within spreading nature, especially a field, the improvement in the homogeneity within the thickness side to Wafer of the diameter of macrostomia is demanded. Thickness measurement can be performed at the a large number point in Wafer as the technique of the ability to check this homogeneity, the standard deviation of each measured value can be taken, and homogeneity can be checked by one 3 times that value of this. It can be said that the homogeneity within a field is high, so that this value is small. As a value, the one of 100 or less 3 times the value of standard deviation is desirable, and 50 or less are more desirable. Moreover, also in the mask manufacture for optical lithography, importance is maximum-attached to CD linearity, and the improvement in the homogeneity within the thickness side in BURANKUSU is demanded.

[0148] The resist constituent of this invention can be filtered after melting to a solvent. Therefore, although the filter used is used in the resist field, it is chosen from inside, and that in which the quality of the material of a filter contains polyethylene, nylon, or polysulfone is specifically used. More specifically, they are the micro guard by Millipore Corp., the micro guard Plus, micro guard MINIKEMU-D, and micro guard MINIKEMU-D. PR, Millipore OBUCHI mizer DEV/DEV-C, Millipore The OBUCHI mizers 16/14, URUCHIBOA N66 by the pole company, POJIDAIN, a nylon falcon, etc. are mentioned. Moreover, what was checked by the following approach can be used about the aperture of a filter. That is, a PSL standard particle (polystyrene latex bead particle diameter of 0.100 micrometers) is distributed in ultrapure water, with a tube pump, continuously, a sink and challenge concentration are measured with a particle counter in the amount of steady flow, and what has been caught 90% or more can be used for a primary filter side as a 0.1 micrometer filter of apertures.

[0149] The positive type electron ray or X ray resist constituent of this invention can be exposed through a predetermined mask after spreading by the suitable methods of application, such as a spinner and a coating machine, on a substrate (example: silicon / diacid-ized silicon covering) which is used for manufacture of a precision integrated circuit device, or the substrate for mask manufacture for optical lithography (example: glass / Cr covering), and a good resist pattern can be obtained by developing negatives by performing BEKU.

[0150] As a developer of the constituent of this invention, a sodium hydroxide, a potassium hydroxide, Inorganic alkali, such as a sodium carbonate, a sodium silicate, a meta-sodium silicate, and aqueous ammonia Primary amines, such as ethylamine and n propylamine, diethylamine, Tertiary amines, such as secondary amines, such as G n butylamine, triethylamine, and methyl diethylamine Alcoholic amines, such as dimethylethanolamine and triethanolamine, Alkaline water solutions, such as annular amines, such as quarternary ammonium salt, such as tetramethylammonium hydroxide and tetraethylammonium hydroxide, a pyrrole, and a piperidine, can be used. Furthermore, alcohols and a surfactant can also be used for the alkaline above-mentioned water solution, carrying out suitable amount addition.

[0151]

[Example] Hereafter, although an example explains this invention to a detail further, thereby, the contents of

this invention are not limited.

[0152] 1. Synthetic pen TAFURORO benzenesulphonyl chloride 25g of the compound (1-1) Pentough Rollo benzenesulfonic acid tetramethylammonium salt which generates an acid with the synthetic example (1) electron ray or X-ray of a configuration material was dissolved in bottom methanol of ice-cooling 100ml, and 100g of tetramethylammonium hydroxide water solutions was slowly added to this 25%. When stirred at the room temperature for 3 hours, the solution of the Pentough Rollo benzenesulfonic acid tetramethylammonium salt was obtained. This solution was used for the salt exchange with sulfonium salt and iodonium salt.

[0153] (1-2) Synthetic diphenyl sulfoxide 50g of triphenylsulfonium Pentough ROROBENZEN sulfonate was dissolved in benzene 800ml, 200g of aluminum chlorides was added to this, and it flowed back for 24 hours. Ice 2L was slowly filled with reaction mixture, 400ml of concentrated hydrochloric acid was added to this, and it heated at 70 degrees C for 10 minutes. After washing and filtering this water solution by 500ml of ethyl acetate, what dissolved 200g of ammonium iodide in 400ml of water was added. When ethyl acetate washed after rinsing, \*\*\*\* and, and the fine particles which deposited were dried, 70g of triphenylsulfonium iodide was obtained. Triphenylsulfonium iodide 30.5g was dissolved in methanol 1000ml, 19.1g of silver oxides was added to this solution, and it stirred at the room temperature for 4 hours. The solution was filtered and the solution of the Pentough Rollo benzenesulfonic acid tetramethylammonium salt of an excessive amount was added to this. Reaction mixture was condensed, this was dissolved in dichloromethane 500ml, and a tetramethylammonium hydroxide water solution and water washed this solution 5%. When the organic phase was condensed after desiccation with anhydrous sodium sulfate, triphenylsulfonium Pentough ROROBENZEN sulfonate (I-1) was obtained.

[0154] (1-3) Synthetic t-amyl benzene 60g [ of JI (4-t-amyl phenyl) iodonium Pentough ROROBENZEN sulfonate ], 39.5g [ of potassium iodates ], 81g [ of acetic anhydrides ], and dichloromethane 170ml was mixed, and 66.8g of bottom concentrated sulfuric acid of ice-cooling was slowly dropped at this. After stirring under ice-cooling for 2 hours, it stirred at the room temperature for 10 hours. 500ml of water was added to reaction mixture under ice-cooling, and when it condensed after it washed this by dichloromethane and a sodium hydrogencarbonate and water washed the extract and the organic phase, the JI (4-t-amyl phenyl) iodonium sulfate was obtained. This sulfate was added to the solution of the Pentough Rollo benzenesulfonic acid tetramethylammonium salt of an excessive amount. 500ml of water was added to this solution, and when it condensed after it washed this by dichloromethane and a tetramethylammonium hydroxide water solution and water washed the extract and the organic phase 5%, JI (4-t-amyl phenyl) iodonium Pentough ROROBENZEN sulfonate (III-1) was obtained. It is compoundable using the same approach as the above about other acid generators.

[0155] (2) Composition of resin (synthetic example 1) It is DMAc about synthetic 4-methoxy-1-naphthol 25g of vinyl ether 1, and chloro ethyl-vinyl-ether 22.9g. It is made to dissolve in 140ml and is NaOH. 6.90g was added and it stirred at 120 degrees C for 2 hours. The NaCl salt was filtered after that, and ethyl acetate and water were added and liquids were separated. Ethyl acetate was distilled out of the organic layer after that, it recrystallized with the methanol, and vinyl ether 1 was obtained at 84% of yield.

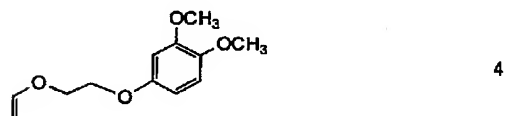
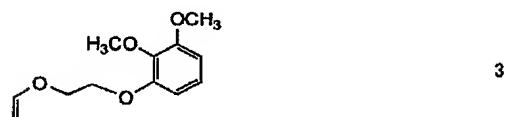
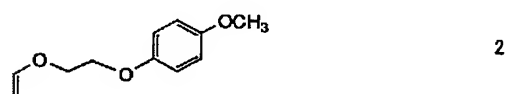
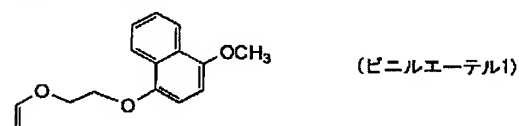
[0156] (Synthetic examples 2-14) Except changing the synthetic \*\*\*\*\* alcohol of vinyl ether 2-14, it reacted like the synthetic example 1 and vinyl ether 2-14 was obtained with silica gel column

chromatography or methanol recrystallization.

[0157] (Synthetic example 15) the inside of the flask in which vinyl ether 15 carried out synthetic desiccation — 9-hydroxymethyl anthracene 25g — anhydrous — THF It was made to dissolve in 100ml and cooled at 0 degree C under the nitrogen air current. 3.17g of sodium hydride was added and it was made to stir for a while. Then, chloro ethyl-vinyl-ether 19.2g was dropped with 0 degree C, and it stirred at the room temperature after dropping termination for 2 hours. After adding a saturated ammonium chloride solution, ethyl acetate and water were added and liquids were separated. The solvent was distilled out of the organic layer after that, the silica gel column chromatography refined, and vinyl ether 15 was obtained at 88% of yield.

[0158]

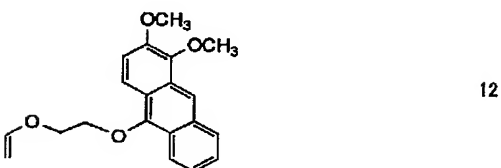
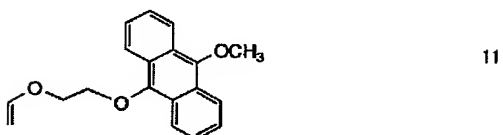
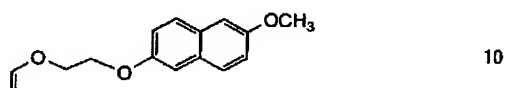
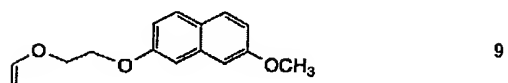
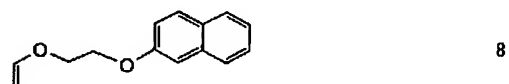
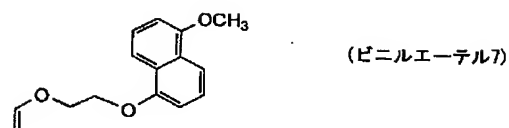
[Formula 55]



[0159]

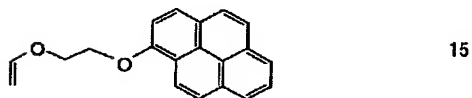
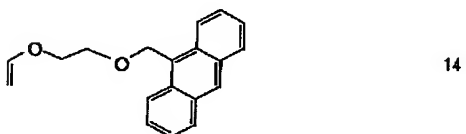
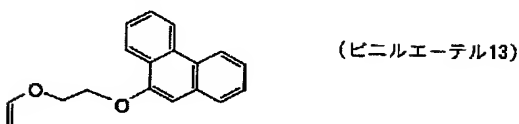
[Formula 56]





[0160]

[Formula 57]



[0161] (Synthetic example 16) The synthetic Nippon Soda Co., Ltd. make of resin 1 and Pori (p-hydroxystyrene) (VP-8000) 50g were dissolved in anhydrous THF200g, 15.25g and 80mg of p-toluenesulfonic acid were added, and vinyl ether 1 was stirred under the room temperature for 18 hours. Dropping and reprecipitation were performed stirring reaction mixture violently in ultrapure water 5L. The obtained resin was dried under 70 degrees C in the vacuum dryer for 12 hours, and resin 1 was obtained. In addition, the weight average molecular weight of VP-8000 made GPC measurement polystyrene the

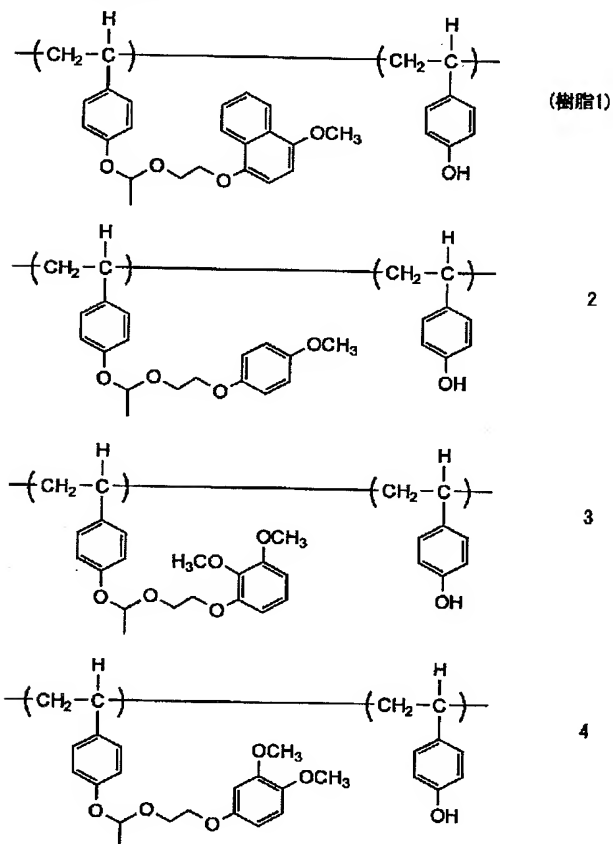
correlation sample, and was 9800.

[0162] (Synthetic examples 17-30) Except changing the vinyl ether to add, it reacted like the synthetic example 16 and resin 2-15 was obtained.

[0163] The resin compounded above is shown below.

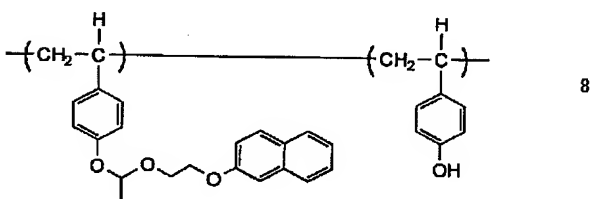
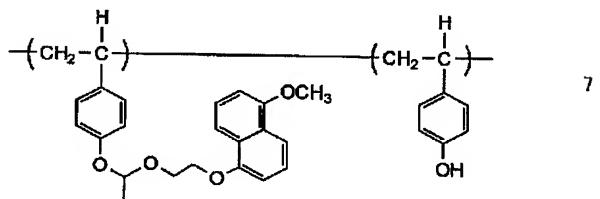
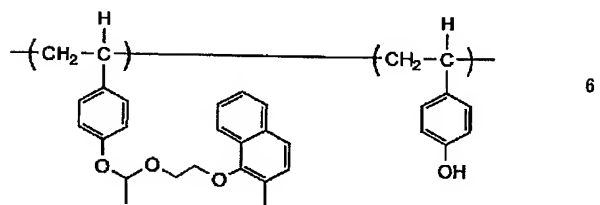
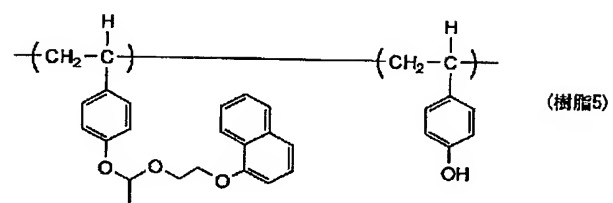
[0164]

[Formula 58]



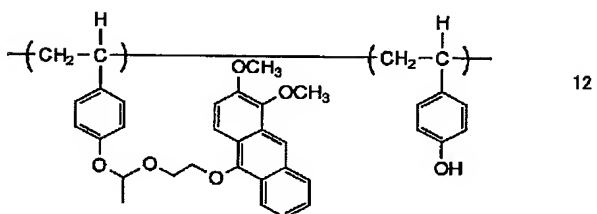
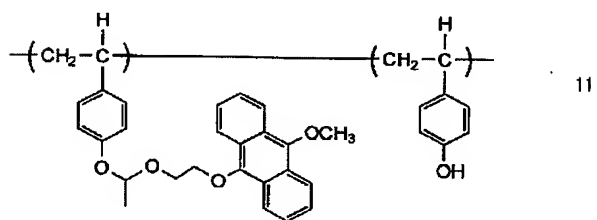
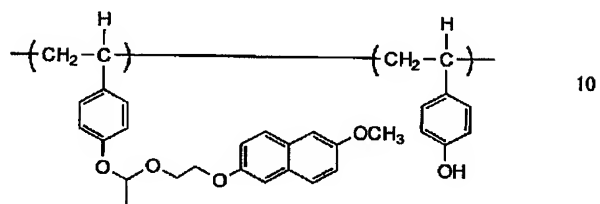
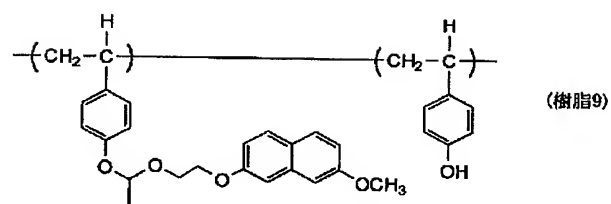
[0165]

[Formula 59]



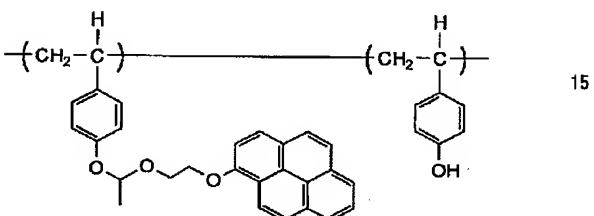
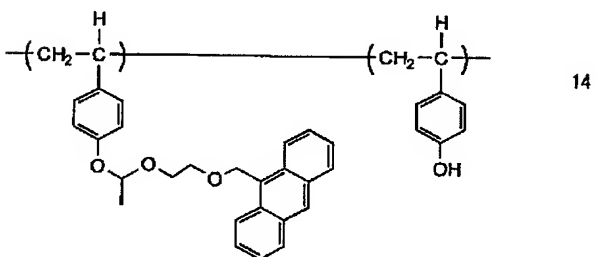
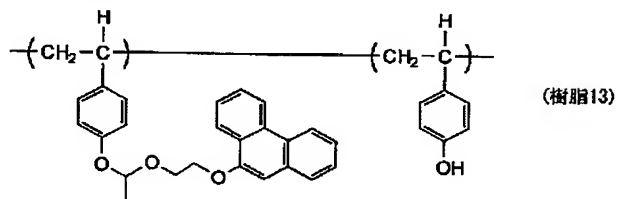
[0166]

[Formula 60]



[0167]

[Formula 61]



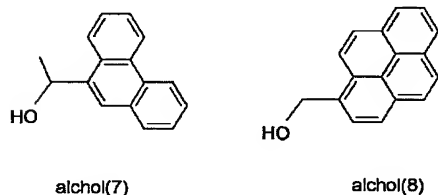
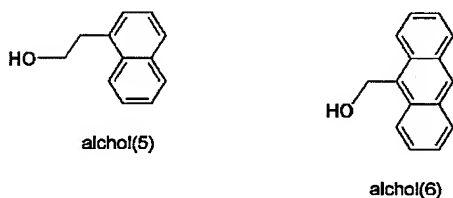
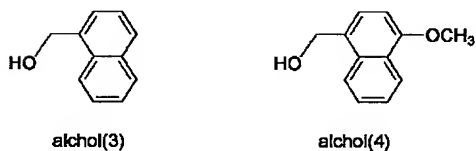
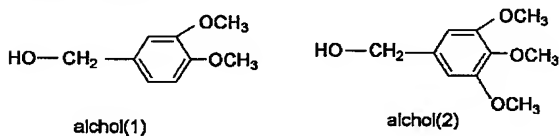
[0168] (Synthetic example 31) Pori (p-hydroxystyrene) the Nippon Soda Co., Ltd. make (molecular weight 8,000) -- 70g was dissolved in propylene glycol methyl ether acetate (PGMEA) 320g, 0.35g of p-toluenesulfonic-acid pyridinium salt was added further, and the heating dissolution was carried out at 60 degrees C. This mixture was decompressed to 60 degrees C and 20mmHg, and about 40g solvent was distilled off with the water which remains in a system. It cooled to 20 degrees C and the addition dissolution of the alcoholic (alcohol) (1) 44.1g of the following structure was carried out. tert-butyl vinyl ether 17.5g was added after that, and churning under 20 degrees C was continued for 5 hours. 280ml of ethyl acetate was added to the reaction mixture, 140 moreml water and a 12ml acetone were added, and extract operation was performed. After repeating rinsing actuation 3 times, it distilled off in 60 degrees C and 20mmHg, and the moisture in a system was removed. Furthermore, the obtained resin solution was diluted with the acetone and white resin was obtained by settling a lot of hexanes. The [resin 16] of the structure which it heats for 24 hours, and 40 degrees C dries by the vacuum dryer, and shows below the resin which repeated this actuation 3 times and was obtained was obtained. Weight average molecular weight was 8,400.

[0169] (Synthetic example 32) - (synthetic example 39)

Except changing the alcohol to add into alcoholic (2) - (8) of the following structure, it reacted like the synthetic example 31 and resin 17-23 was obtained.

[0170]

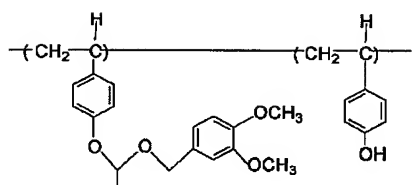
[Formula 62]



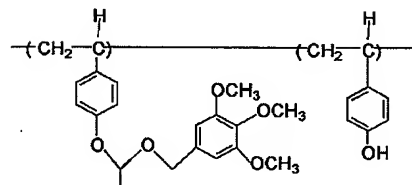
[0171]

[Formula 63]

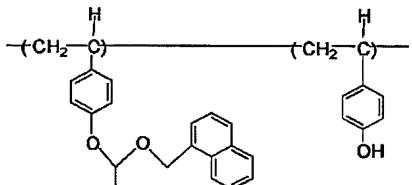
樹脂16



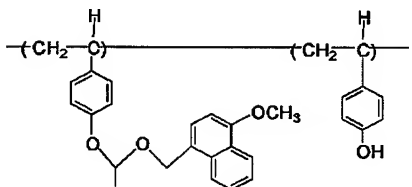
樹脂17



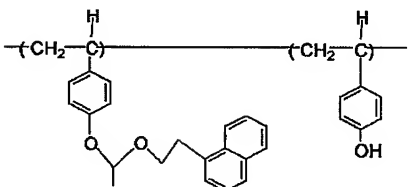
樹脂18



樹脂19



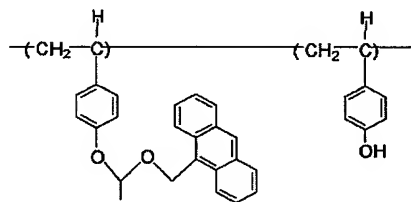
樹脂20



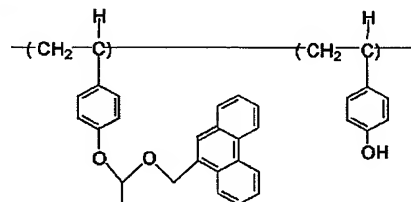
[0172]

[Formula 64]

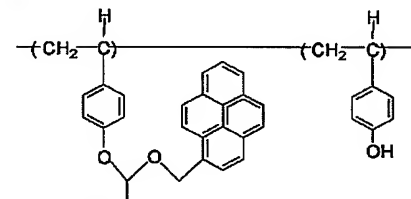
樹脂21



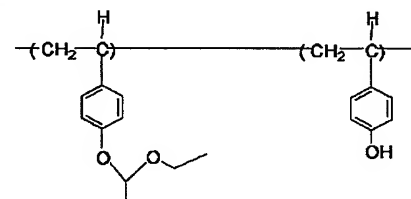
樹脂22



樹脂23



樹脂24 (比較用)



[0173] The Ip value of the HO-X corresponding point in the formula (I) which the above-mentioned resin has is as follows. The product made from Oxford Molecular, and software-CAChe4.1.1 It computed using MOPAC (PM3 parameter). (Unit: eV)

Resin 1: 8.237 Resin 2: 8.717 Resin 3: 8.783 Resin 4: 8.505 Resin 5: 8.543 Resin 6: 8.469 Resin 7: 8.293 Resin 8: 8.722 Resin 9: 8.715 Resin 10: 8.477 resin 11: 7.698 Resin 12: 8.029 Resin 13: 8.500 resin 14: 8.109 Resin 15: 8.015 resin 16: 8.588 resin 17: 8.608 Resin 18:8.739 Resin 19: 8.413 Resin 20: 8.746 resin 21: 8.109 Resin 22: 8.851 Resin 23:8.182 Resin 24:10.890 (compound ethanol for count) for a comparison

[0174] Moreover, the ratio and weight average molecular weight of a repeat unit which have the balking radical of each resin are shown below.

[0175]

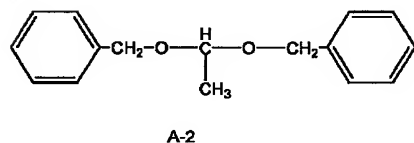
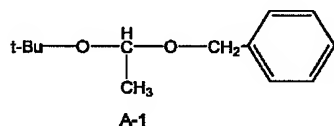
[Table 1]

樹脂	離脱基を有する 繰返し単位の 比率(mol%)	重量平均分子量
樹脂 1	14.8	9800
樹脂 2	14.2	9800
樹脂 3	13.3	9700
樹脂 4	14.5	9800
樹脂 5	13.1	9600
樹脂 6	14.2	9700
樹脂 7	14.7	9400
樹脂 8	14.4	9700
樹脂 9	13.4	9500
樹脂 10	14.2	9800
樹脂 11	13.1	9600
樹脂 12	13.8	9400
樹脂 13	13.5	9200
樹脂 14	13.2	9700
樹脂 15	13.4	9900
樹脂 16	16.7	9800
樹脂 17	16.2	9800
樹脂 18	15.3	9800
樹脂 19	15.0	9700
樹脂 20	15.6	9800
樹脂 21	16.1	9700
樹脂 22	15.9	9700
樹脂 23	15.7	9700
比較用樹脂	14.6	9500

[0176] (Synthetic example 40) Benzyl alcohol 54.1g and p-toluenesulfonic acid It is PGMEA about 0.4g. It dissolved in 230g, 60 degrees C and reduced pressure-under 20mmHg distilling off were performed, and the water in a system was removed. The fraction was about 18g. After cooling to 20 degrees C, tert-butyl vinyl ether 50.1g was added and churning was performed for 1 hour. After adding and agitating 0.4g triethylamine to a reaction mixture, 200ml of ethyl acetate was added and 100ml water performed the rinsing extract. After repeating this rinsing process 3 times, reduced pressure distilling off of the ethyl acetate was carried out, and the acetal compound A -1 and A-2 mixture were obtained. This mixture was isolated by silica gel column chromatography.

[0177]

[Formula 65]



[0178] (Synthetic example 41) The acetal compound A -three to A-12 was obtained by the same approach as the synthetic example 40 using the alcoholic compound shown below instead of benzyl alcohol.

[0179]

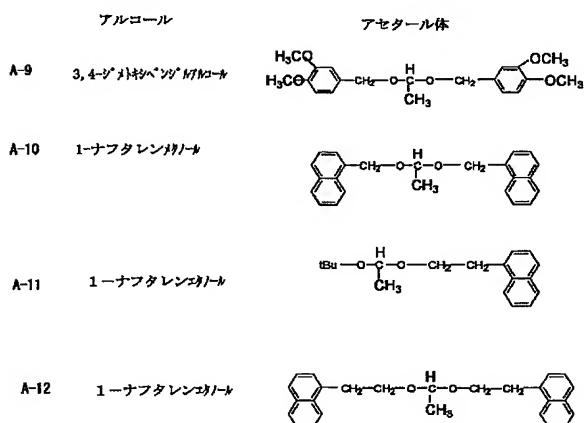
[Table 2]



	アルコール	アセタール体
A-3	フェネチルアルコール	
A-4	フェノキシアルコール	
A-5	ビベロニルアルコール	
A-6	シクロヘキシルエタノール	
A-7	4-ヒドロキシ-2-ブタノン	$\text{Ac-O-CH}_2\text{CH}_2\text{-O-}\underset{\text{CH}_3}{\underset{ }{\text{C}}}\text{-O-CH}_2\text{CH}_2\text{-O-Ac}$ Ac: アセチル基
A-8	2-ノルボルナンメタノール	

[0180]

[Formula 66]



[0181] 2. Example [Examples 1-23 and Examples 1 and 2 of Comparison]

(1) The painting resin 1 (12g) of a resist, the acid generator (I-1) (0.11g), the nitrogen-containing basicity compound B-1 (0.0065g), the surfactant W-1 (0.0022g), and the acetal compound (A-9) (addition given in Table 3) were dissolved in propylene-glycol-monomethyl-ether acetate 19.5g, this was filtered with the 0.1-micrometer Teflon (trademark) filter, and the resist solution of an example 1 was prepared. Similarly, as shown in Table 3, the class of each component was changed, and the resist solution of examples 2-23 and the examples 1 and 2 of a comparison was prepared. Each sample solution was applied on the silicon wafer using the spin coater, for 120 degrees C and 90 seconds, it dried with the hot plate of a vacuum adsorption mold, and the resist film of 0.5 micrometers of thickness was obtained.

[0182] (2) The resist film of \*\*\*\*\* of a resist pattern was irradiated by using electron-beam-lithography equipment (pressurization electrical potential difference of 50kV). It heated with the vacuum adsorption mold hot plate after the exposure, respectively (it is 60 seconds at 110 degrees C), and was immersed for 60 seconds in the tetramethylammonium hydroxide (TMAH) water solution 2.38%, and for 30 seconds, with water, the rinse was carried out and it dried. The cross-section configuration of the obtained contact hole pattern, Rhine, and a tooth-space pattern was observed with the scanning electron microscope.

[0183] (3) Sensibility and the evaluation sensibility of resolution made sensibility the minimum exposure when resolving 0.20-micrometer Rhine (Rhine: tooth-space =1:1), and made resolution marginal resolution (Rhine and a tooth space are separation resolving) in the exposure. Resolution of the thing which 0.20-micrometer Rhine (Rhine: tooth-space =1:1) does not resolve, therefore a limitation was made into resolution, and the exposure at that time was made into sensibility.

[0184] The upper part (top) and a pars basilaris ossis occipitalis (bottom) estimated the Rhine width of face of 0.2-micrometer Rhine (Rhine: tooth-space =1:1) according to the difference of the Rhine width of face of the observe top and a bottom at the evaluation scanning electron microscope of the Rhine width of face in the pattern top and a bottom. It evaluated [ what / 0.2 micrometer Rhine (Rhine: tooth-space =1:1) does not resolve ] about the Rhine width of face in the resolution of a limitation.

O : the difference of the Rhine width of face of the top section and the bottom section is less than (% to the Rhine width of face of the bottom section) 3%.

O : the difference of the Rhine width of face of the top section and the bottom section is less than (% to the Rhine width of face of the bottom section) 5%.

x: The difference of the Rhine width of face of the top section and the bottom section is 5% or more (% to the Rhine width of face of the bottom section).

[0185]

[Table 3]

	樹脂	アセタール化合物 (添加量: wt%) *	酸発生 剤	含硫素塩基 性化合物	界面活 性剤
実施例 1	1	A-9 (7%)	I-1	B-1	W-1
実施例 2	2	A-10 (12%)	I-7	B-2	W-2
実施例 3	3	A-11 (8%)	I-8	B-3	W-3
実施例 4	4	A-12 (15%)	I-9	B-4	W-4
実施例 5	5	A-1 (5%)	I-13	B-5	W-1
実施例 6	6	A-2 (7%)	I-16	B-5	W-2
実施例 7	7	A-3 (7%)	I-21	B-4	W-3
実施例 8	8	A-4 (10%)	II-1	B-3	W-4
実施例 9	9	A-6 (12%)	III-1	B-2	W-5
実施例 10	10	A-6 (8%)	I-1	B-1	W-1
実施例 11	11	A-7 (9%)	I-7	B-2	W-2
実施例 12	12	A-8 (5%)	I-8	B-3	W-3
実施例 13	13	A-9 (10%)	I-9	B-4	W-4
実施例 14	14	A-10 (8%)	I-13	B-5	W-5
実施例 15	15	A-11 (7%)	I-16	B-1	W-2
実施例 16	16	A-9 (9%)	I-21	-	W-1
実施例 17	17	A-10 (15%)	II-1	-	W-3
実施例 18	18	A-11 (8%)	III-1	-	W-4
実施例 19	19	A-12 (5%)	I-1	-	W-5
実施例 20	20	A-5 (10%)	I-7	-	W-5
実施例 21	21	A-9 (10%)	I-8	B-1	
実施例 22	22	A-7 (10%)	I-9	B-2	
実施例 23	23	A-9 (5%)	I-13	-	
比較例 1	24	A-10 (9%)	I-7	B-2	W-2
比較例 2	1	添加せず	I-1	B-1	W-1

\*アセタール化合物の添加量「wt%」は、樹脂の添加量 (12 g) を 100 とした場合の重量%

[0186] The cable address used in Table 3 shows the following contents.

[0187] About an organic base nature compound, it is as follows.

B-1: 2, 4, 5-triphenyl imidazole B-2:1, 5-diazabicyclo [4.3.0] nona-5-en B-3:4-dimethylamino pyridine B-4:1, and 8-diazabicyclo [5.4.0] undeca-7-en B- 5:N-cyclohexyl-N'-morpholino ethyl thiourea [0188] About a surfactant, it is as follows.

W-1: Troysol S-366 (made in Troy Chemical)

W-2: Megger fuck F176 (Dainippon Ink make)

W-3: Megger fuck R08 (Dainippon Ink make)

W-4: Polysiloxane polymer KP-341 (Shin-Etsu Chemical Co., Ltd. make)

W-5: Sir chlorofluocarbon S-382 (Asahi Glass Co., Ltd. make)

[0189]

[Table 4]

	感度 ( $\mu\text{C}/\text{cm}^2$ )	解像力 ( $\mu\text{m}$ )	トップ/ボトムライン 幅差
実施例 1	0.5	0.04	◎
実施例 2	0.5	0.04	◎
実施例 3	0.7	0.05	◎
実施例 4	0.8	0.04	◎
実施例 5	0.7	0.05	◎
実施例 6	0.8	0.04	◎
実施例 7	0.9	0.05	◎
実施例 8	0.6	0.05	◎
実施例 9	0.7	0.04	◎
実施例 10	0.9	0.04	◎
実施例 11	1.0	0.04	◎
実施例 12	0.6	0.04	◎
実施例 13	0.5	0.05	◎
実施例 14	0.5	0.04	◎
実施例 15	0.6	0.04	◎
実施例 16	1.0	0.06	○
実施例 17	1.1	0.06	○
実施例 18	1.2	0.05	○
実施例 19	1.3	0.05	○
実施例 20	1.1	0.06	◎
実施例 21	1.6	0.06	◎
実施例 22	1.7	0.06	◎
実施例 23	1.9	0.07	○
比較例 1	4.5	0.12	○
比較例 2	1.0	0.05	×

[0190] From the result of Table 4, the positive-resist constituents of this invention are high sensitivity and high resolution, and are understood that the pattern profile obtained is good.

[0191] In examples 1-23, when the solvent was changed into propylene-glycol-monomethyl-ether acetate / propylene-glycol-monomethyl-ether =80 / 20 (weight ratio) and was carried out similarly, the same effectiveness was acquired.

[0192] (4) The resist film of 0.40 micrometers of thickness was obtained by the same approach as the above (1), using respectively each resist constituent of the patterning above-mentioned examples 1 and 20 and the examples 1 and 2 of a comparison by actual size X-ray lithography. Subsequently, except having used the actual size X-ray aligner (gap value; 20nm), patterning was performed like the above (2) and the same approach as the above (3) estimated the resist engine performance. An evaluation result is shown in Table 5.

[0193]

Table 5 resist constituent Sensibility (mJ/cm<sup>2</sup>) Resolving power (micrometer) Rhine width difference of the top/bottom Example 1 40 0.09 O Example 20 35 0.10 O Example 1 of a comparison 130 0.16 O Example 2 of a comparison 70 0.12 x [0194] It turns out that the engine performance in which the resist constituent of this invention was extremely excellent also in X-ray lithography is shown so that more clearly than the above-mentioned table 5. [0195]

[Effect of the Invention] The electron ray of this invention or the positive-resist constituent for X-rays is high sensitivity and high resolution, and its resist pattern obtained is good.

[Translation done.]